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POWER PLANT COOLING WATER DISCHARGES IN NORTHERN CALIFORNIA

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In-plant studies were conducted during chlorination cycles to determine oxidant residuals at both the condenser inlets and at a point near the outfall. Both free and total oxidant residuals were measured amperometrically for most studies. The DPD-FAS method was included in later studies to gain a better understanding of the nature of the oxidant residual. These results indicated that most of the oxidant residual at the Hunters Point and Moss Landing power plants was bromine residual.

Decay studies were conducted at the plant sites on the chlorinated cooling water collected at the outfall. The slowest decay was observed at the Contra Costa plant where the cooling water was the freshest. The most rapid decay was at the Hunters Point plant. The presence of sunlight increased the rate of decay at all locations.

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POWER PLANT COOLING WATER CHLORINATION IN NORTHERN CALIFORNIA

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory (CERL).

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects, and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report adds significantly to our understanding of residual chlorine behavior in coastal waters. From this work power plants may be able to restructure their disinfection programs and reduce the amount of chlorine reaching the environment as well as reducing costs. Regulatory programs may be able to use the results to improve effluent guidelines and monitoring programs.

PREFACE

The concern for the potential toxicity of chlorinated effluents to receiving waters biota pampered the study of the nature and persistence of oxidant residuals in power plant cooling water. The study was designed to provide field information from operating power plants so that actual operating levels of residual and their persistence could be defined. The investigation was directed towards power plants close to the San Francisco Bay Area and located on estuarine of coastal waters.

ABSTRACT

This research program was designed to determine the nature, levels, and persistence of "chlorine" residuals in the cooling water effluents of power plants located in and around the San Francisco Bay Area. Plants were located at Potrero and Hunters Point (San Francisco Bay), Contra Costa (San Joaquin River), Pittsburg (Suisun Bay), and Moss Landing (Monterey Bay).

A survey was conducted of chlorination practices at five power plants owned and operated by the Pacific Gas and Electric Company. Frequency and duration of chlorination varied significantly from plant to plant and was controlled analytically by the orthotolidine and/or amperometric methods. All the plants plan to change to using the amperometric method for future control purposes.

In-plant studies were conducted during chlorination cycles to determine oxidant residuals at both the condenser inlets and at a point near the outfall. Both free and total oxidant residuals were measured amperometrically for most studies. The DPD-FAS method was included in later studies to gain a better understanding of the nature of the oxidant residual. These results indicated that most of the oxidant residual at the Hunters Point and Moss Landing power plants was bromine residual.

Decay studies were conducted at the plant sites on the chlorinated cooling water collected at the outfall. The slowest decay was observed at the Contra Costa plant where the cooling water was the freshest. The most rapid decay was at the Hunters Point plant. The presence of sunlight increased the rate of decay at all locations.

Receiving water studies detected maximum total oxidant residuals at the surface. The distances from the outfall structures to the 0.02 mg/ℓ total oxidant isoconcentration line were determined at three power plants. Total oxidant residuals were measured at the surface of Monterey Bay above a submerged outfall structure. Toxicity of receiving water oxidant residual levels was predicted.

This report was submitted in fulfillment of Grant No. R803959 by the Sanitary Engineering Research Laboratory under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 31, 1975 to December 31, 1976, and work was completed as of June 30, 1977.

CONTENTS

Foreword iii

Preface iv

Abstract v

Figures viii

Tables x

Abbreviations and Symbols xi

Acknowledgment xii

1. Introduction 1

2. Material and Methods 2

3. Results 13

4. Discussion 37

5. Conclusions 44

References 46

Appendix 1 Field Data 48

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FIGURES

Number		Page
1	Power plant locations	3
2	Contra Costa power plant	5
3	Pittsburg power plant	6
4	Hunters Point power plant	7
5	Potrero power plant	8
6	Moss Landing power plant	9
7	Laboratory comparison of DPD-FAS titrimetric and amperometric titration methods	23
8	Percentage loss of TOR between the COND-IN and the outfall sampling point for various power plants	24
9	Results of decay studies conducted at the Contra Costa power plant, units 6 and 7 outfall	26
10	Results of decay studies conducted at the Hunters Point power plant, unit 4 outfall	27
11	Results of decay studies conducted the the Potrero power plant, unit 3 outfall	28
12	Results of decay studies conducted at the Moss Landing power plant, units 6 and 7 at ISE	29
13	TOR ($mgCl_2/\ell$) at the surface of the receiving water at the Contra Costa power plant, units 6 and 7	31
14	TOR ($mgCl_2/\ell$) at receiving water surface at the Hunters Point power plant, unit 4	32
15	TOR ($mgCl_2/\ell$) at receiving water surface at the Potrero power plant, unit 3	33
16	TOR ($mgCl_2/\ell$) at receiving water surface at the Potrero power plant, units 1 and 2	34
17	FOR ($mgCl_2/\ell$) at the receiving water surface at the Moss Landing power plant, unit 6	35
18	Time required for 99% conversion of free chlorine to HOBr at 25°C and a pH of 8.3	38
19	Principal species of bromine and bromamine after 1-2 min at various pH and ammonia to bromine ratios	40
20	In-plant study at the Contra Costa power plant 20 Jan 1976, unit 6, condenser #11	49
21	In-plant study at the Contra Costa power plant 10 Feb 1976, unit 7, condenser #14	50
22	In-plant study at the Contra Costa power plant 6 Jun 1976, unit 7, condenser #13	51
23	In-plant study at the Contra Costa power plant 14 Sep 1976, unit 6, condenser #11	52
24	In-plant study at the Hunters Point power plant, 16 Dec 1975, unit 4	53

FIGURES (continued)

Number		Page
25	In-plant study at the Hunters Point power plant, 17 May 1976, unit 4	54
26	In-plant study at the Hunters point power plant, 26 Aug 1976, unit 4	55
27	In-plant study at the Potrero power plant, 23 Feb 1976, unit 3, N. condenser	56
28	In-plant study at the Potrero power plant, 4 Mar 1976, unit 3, N. condenser	57
29	In-plant study at the Moss Landing power plant, 12 Apr 1976, unit 7	58
30	In-plant study at the Moss Landing power plant, 19 Apr 1976, unit 7	59
31	In-plant study at the Moss Landing power plant, 14 Jul 1976, unit 6	60
32	In-plant study at the Moss Landing power plant, 14 Jul 1976, unit 7	61
33	In-plant study at the Moss Landing power plant, 22 Jul 1976, unit 6	62
34	In-plant study at the Moss Landing power plant, 5 Aug 1976, unit 7	63
35	In-plant study at the Moss Landing power plant, 23 Sep 1976, unit 6	64

TABLES

Number		Page
1	Power plant operating data	2
2	Chlorination practices at PG&E power plants	10
3	Summary of field study results at Contra Costa power plant, units 6 and 7	14
4	Water quality and tidal data at the Contra Costa power plant	15
5	Summary of field study results at the Hunters Point Power plant (unit 4) and Potrero power plant (unit 3)	17
6	Water quality and tidal data at the Hunters Point and Potrero power plants	18
7	Summary of field study results at the Moss Landing power plant, units 6 and 7	19
8	Water quality and tidal data at the Moss Landing power plant	20
9	Summary of loss of oxidant residual within the power plant cooling water system	25
10	Summary of decay studies	30
11	Acute and chronic doses of chlorine to marine freshwater organisms (Mattice and Ziettel) (3)	42

ABBREVIATIONS AND SYMBOLS

COND-IN -- Condenser inlet sampling point

COND-OUT -- Condenser outlet sampling point

DPD -- N,N-diethyl-p-phenylenediamine

FAS -- Ferrous ammonium sulfate

FOR -- Free oxidant residual, $mgCl_2/\ell$

INJ-PT -- Chlorine injection point

ISE -- Sampling point at International Shellfish Enterprises, Inc.

MW -- Megawatt

OT -- Orthotolidine method

OUT -- Outfall sampling point

PAO -- Phenylarsine oxide

PG&E -- Pacific Gas and Electric Company

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SECTION I

INTRODUCTION

Power plants require large volumes of cooling water to carry away waste heat. Bacterial and algal slimes will attach themselves to the walls of the piping and decrease the heat transfer across the condensers if fouling is not controlled. The most economical method currently used to control fouling is the addition of chlorine to the cooling water.

Chlorine presents problems when its toxic effects carry over into receiving waters. Brungs (1) conducted a comprehensive review of the literature dealing with chlorine toxicity to freshwater fish for both continuous and intermittent treatment. Based on these studies he recommended intermittent chlorine limits in the discharge of power plants that vary from 0.2 mg/ℓ to 0.04 mg/ℓ total residual for up to 2 hr per day depending on the degree of protection desired. Basch and Truchan (2) studied the effect of intermittent chlorination on brown trout (Salmo trutta) at five Michigan power plants. They found the 48-hr total residual chlorine intermittent concentrations lethal to 50 percent of the brown trout to range from 0.14 to 0.17 mg/ℓ and 0.18 to 0.19 mg/ℓ for fish exposed to two and four 30 min chlorination cycles, respectively. Mattice and Zittel (3) conducted a comprehensive review of the literature dealing with the toxicity of chlorine to both freshwater and marine organisms. Based on this research they determined both acute and chronic toxicity thresholds and conclude that marine organisms appear more susceptible to acute doses of chlorine whereas freshwater organisms appear more susceptible to chronic concentrations.

The increasing awareness of the toxicity of chlorine residuals has prompted regulatory control of chlorine discharges in power plant cooling waters. The Environmental Protection Agency has established free chlorine discharge guidelines of 0.5 mg/ℓ maximum and 0.2 mg/ℓ average concentration for up to two hours per day from any one unit (4). The California Central Coast Regional Water Quality Control Board has set daily maximum limits of 0.02 mg Cl_2/ℓ undissociated free available chlorine and 0.1 mg Cl_2/ℓ total available chlorine in power plant discharges (5). The San Francisco Bay Regional Water Quality Control Board has set even stricter limitations of an instantaneous maximum chlorine residual of 0.0 mg/ℓ (6).

This study was conducted to determine the nature, levels, and persistence of chlorinated compounds in the discharges of five power plants in Northern California. In-plant studies were conducted to understand the demands for chlorine in the cooling water system and to determine the levels reaching the receiving waters. Decay studies conducted at the outfalls together with measurements of oxidant residuals in the receiving water provide a base for estimating the persistence and zone of influence of the chlorinated compounds.

SECTION 2

MATERIAL AND METHODS

POWER PLANT LOCATION AND DESCRIPTION

A map showing the location of the five power plants studied is presented in Figure 1. Water quality varied from fresh at Contra Costa to marine at Moss Landing.

A summary of the operating data for each plant is presented in Table 1. All the plants have the capability of burning either fuel oil or natural gas. The plants rarely operated at maximum capacity. Usually the newer, more efficient units in any plant operated continuously and the older units were used during peak demand periods and during periodic shutdowns of the other units.

TABLE 1. POWER PLANT OPERATING DATA

POWER PLANT	GROSS GENERATING CAPACITY (MW)	NO. OF UNITS	SOURCE OF INTAKE WATER	COOLING WATER FLOWRATE*	
				(m^3/sec)	(gpm)
Contra Costa	1300	7	San Joaquin River	43.2	684,000
Pittsburg	2060	7†	Suisun Bay	45.4	720,000
Hunters Point	400	3	San Francisco Bay	18.2	288,000
Potrero	330	3	San Francisco Bay	16.5	262,000
Moss Landing	2110	7	Monterey Bay	63.1	1,000,000

*All units in operation.

†Unit 7 cooled by a spray canal.

Figure 1. Power plant locations.

Plan diagrams of the once-through cooling water systems at each of the power plants are presented in Figures 2 to 6. Cooling water is diverted from its source and pumped through the cooling system by circulating water pumps located at the intake structures. The cooling water first passes through bar racks which prevent large objects from entering the system. Smaller objects are removed by travelling screens which rotate periodically and are cleaned with high pressure water.

Heat exchange between cooling water and saturated steam occurs in the condensers which consist of bundles of 22.2 mm (7/8 in.) or 25.4 mm (1 in.) diameter aluminum-brass or copper-nickel alloy tubes. There is one condenser per unit which is divided into two halves. The heated flows of cooling water combine immediately after the condenser and are discharged to the receiving water at the outfall structure.

Cooling water sampling locations are indicated for each power plant in Figures 2 to 6. Cooling water could generally be sampled at the condenser inlets (COND-IN), condenser outlets (COND-OUT), and at outfall manholes (OUT) Very convenient sample taps had been set up at the COND-IN because this was where oxidant residuals were routinely measured by plant operating personnel. Sampling at the COND-OUT was more difficult even though taps generally existed or were readily installed because samples had to be pumped out against a vacuum of about 25.4 cm (10 in.) of mercury. Outfall manholes generally existed as part of a discharge structure so that samples taken from these manholes were representative of the water being discharged to the receiving water. At Moss Landing, Units 6 and 7 discharged into Monterey Bay, 242 m (800 ft) off shore, at a depth of 6.1 m (20 ft). A sampling point approximately midway between the condensers and the outfall was furnished by the International Shellfish Enterprises, Inc. (ISE).

CHLORINATION PRACTICES

Chlorine is injected intermittently into the cooling water flow to control slime-causing organisms. In PG&E plants, liquid chlorine is withdrawn from one-ton cylinders, evaporated, and injected into a water line to produce a concentrated chlorine solution. This solution flows to the point of injection in a well behind the travelling screens and in front of the circulating water pumps. Oxidant residuals are routinely measured at the COND-IN and the chlorine injection rate is adjusted to give the desired residual. These adjustments are rarely needed on a daily basis, however the residual monitoring is important to insure proper operation of the chlorinators which are somewhat unreliable when subjected to the frequent startups and shutdowns encountered in intermittent chlorination.

A summary of chlorination practices for the newest units at each of the five PG&E power plants is presented in Table 2. The newest units were chosen for study because they were the largest and most frequently operated. A great deal of variation in frequency, duration, and levels of chlorination existed. Frequency varied from 1/week to 4/day and was changed during the year to meet changing demands. Duration of chlorination ranged from 15 to 40 min. All the plants seek to maintain a 0.5 mg/ℓ residual at the COND-IN

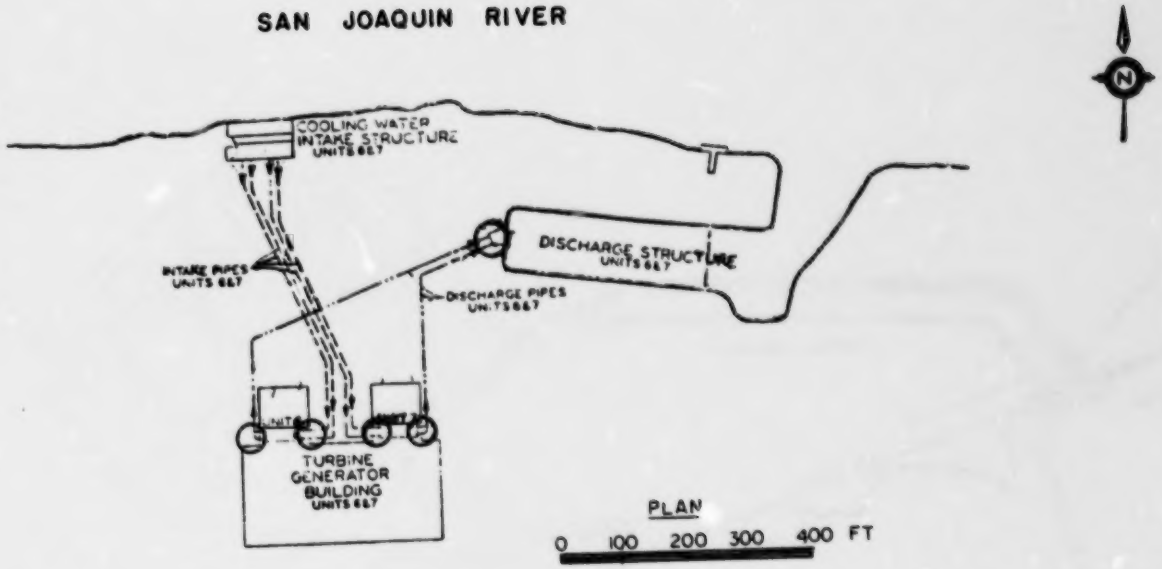

Figure 2. Contra Costa Power Plant.

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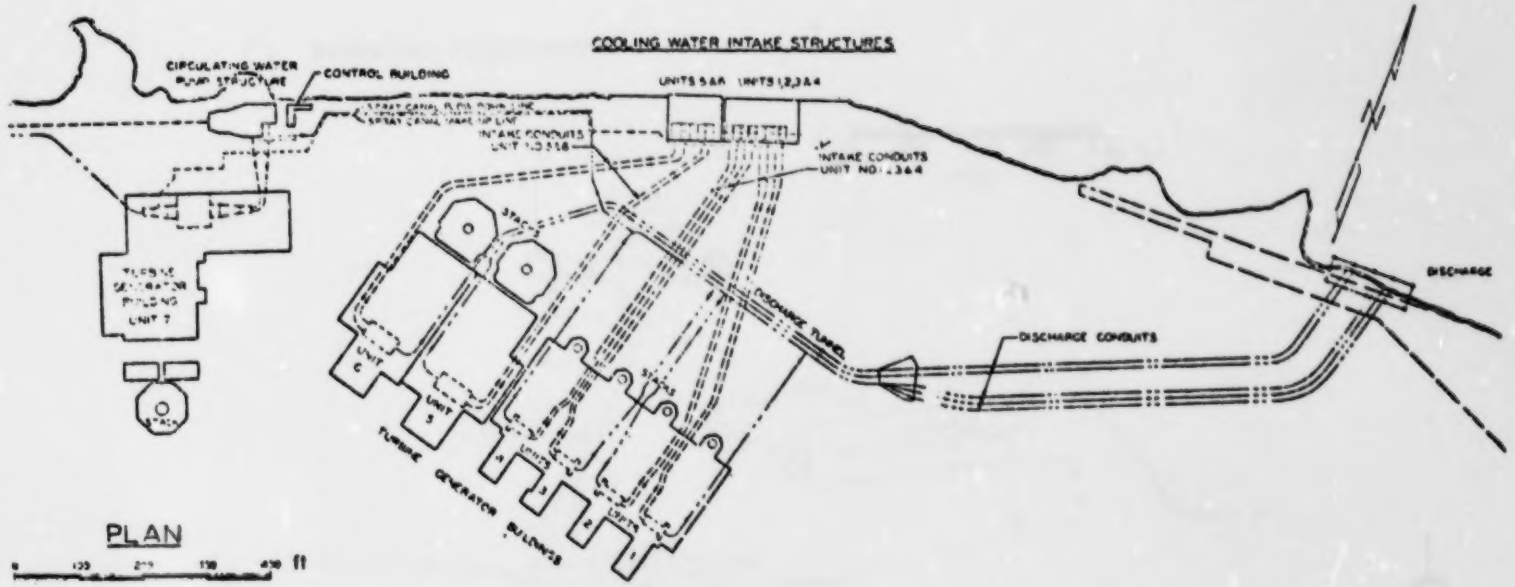

Figure 3. Pittsburg Power Plant.

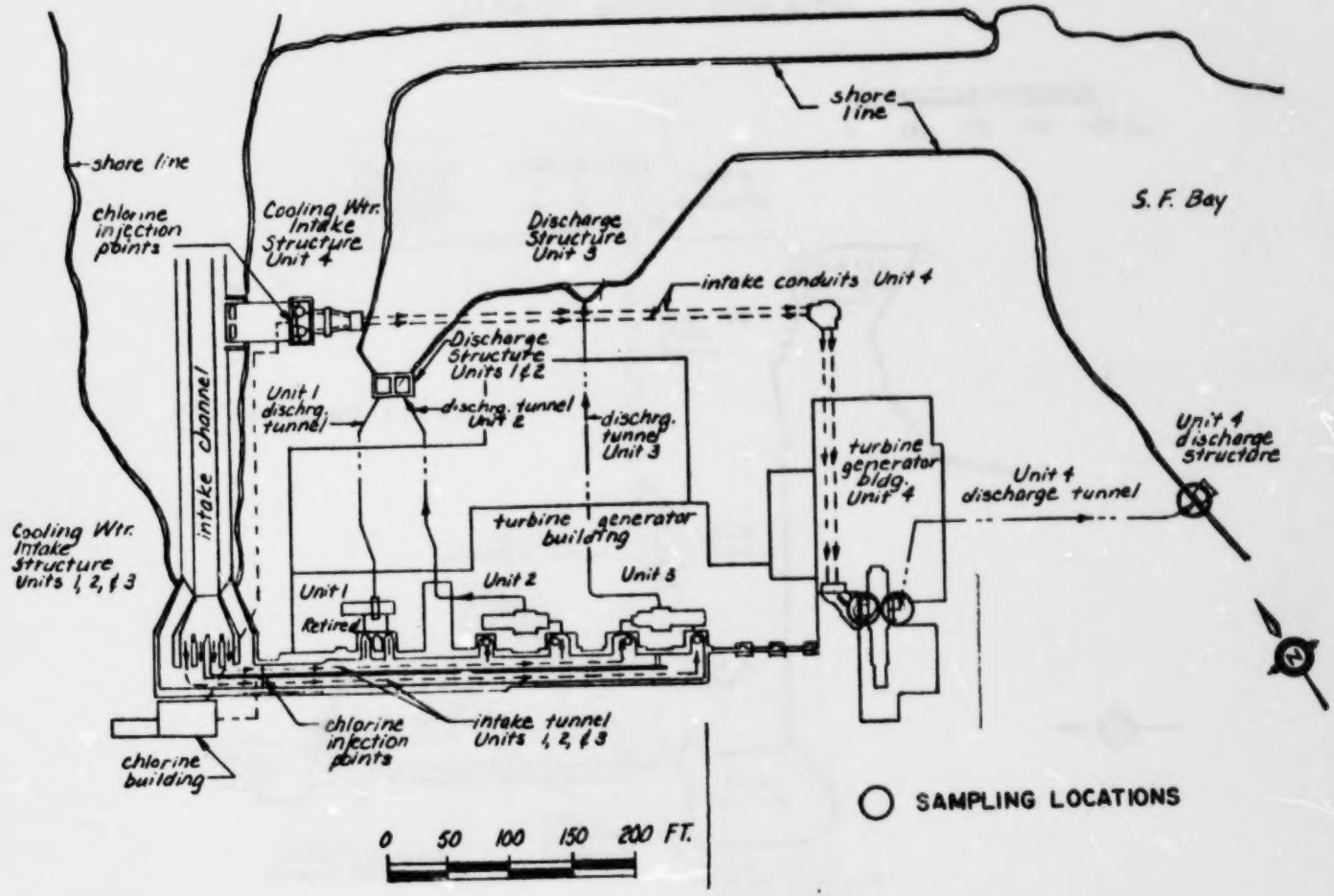

Figure 4. Hunters Point Power Plant.

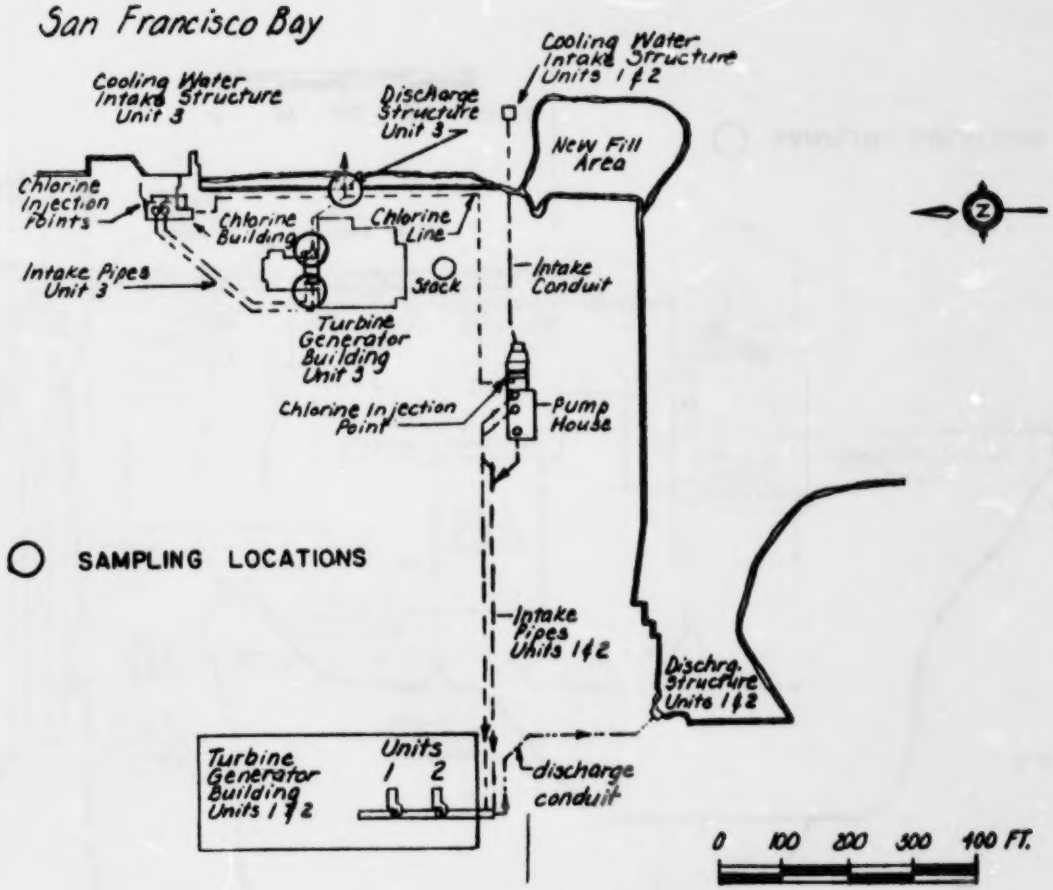

Figure 5. Potrero Power Plant.

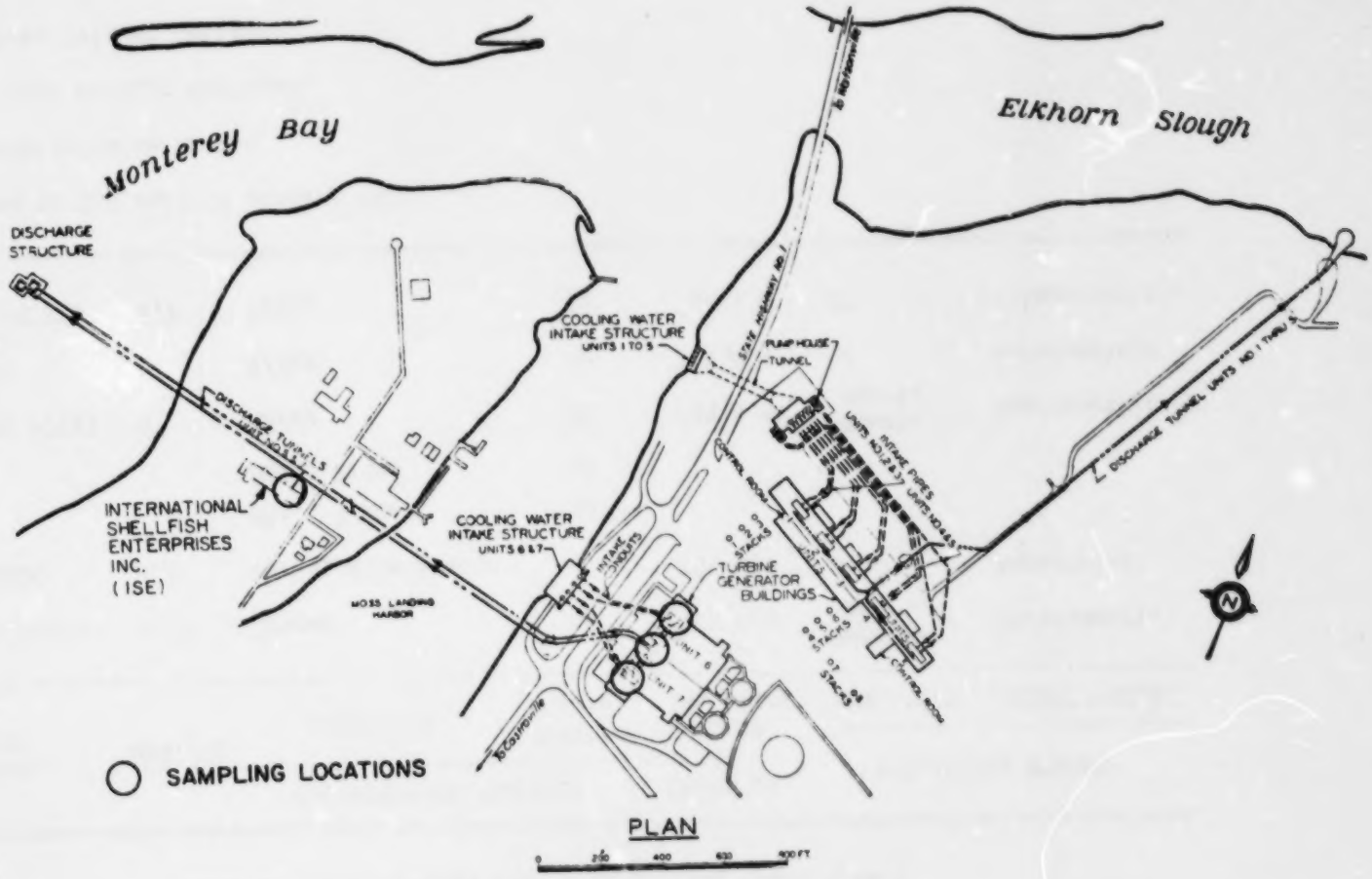

Figure 6. Moss Landing Power Plant.

TABLE 2. CHLORINATION PRACTICES AT PG&E POWER PLANTS

POWER PLANT	UNIT(S)	CHLORINATION SCHEDULE		CRITERIA AT COND-IN (mg Cl_2/ℓ)	ANALYTICAL METHOD	
		FREQUENCY	DURATION (min)		NOV. 1975	CURRENT/FUTURE
CONTRA COSTA	6,7	1/week	40	TOR,0.5	Amperometric	Amperometric
PITTSBURG	5,6	Varies with Season		TOR,0.5	OT	Amperometric
		Min., 1/week	30			
		Max., 1/day	30			
HUNTERS POINT	4	4/day	30	FOR,0.5*	Amperometric	Amperometric
POTRERO	3	2/day	30	TOR,0.5*	OT	Amperometric
MOSS LANDING	6,7	1/day	15	TOR,1.0	OT	OT/Amperometric

*Lowered to 0.4 mg/ℓ in January 1977.

OT = Orthotolidine Method.

TOR = Total Oxidant Residual.

FOR = Free Oxidant Residual.

except for Moss Landing where a 1.0 mg/ℓ residual for a shorter duration was used. Hunters Point was the only plant to measure a free residual and use it as their criterion for dosing. The orthotolidine (OT) method was used at all the plants until recently because it was the most portable and was the easiest for the operators to learn and use. All the plants are currently using or are in the process of changing over to the amperometric titration method.

FIELD STUDY PROCEDURES

In-Plant Studies

Field studies were conducted at four of the power plants. No studies were conducted at the Pittsburg plant because no convenient sampling point existed near the outfall. Studies were conducted during normal chlorination cycles and were designed to monitor existing chlorination practices, therefore no changes were made in chlorine injection rate, duration, or frequency of chlorination cycles to accommodate this work.

At the beginning of the study, oxidant residuals were determined solely by the amperometric method. During the course of the investigation, the DPD-FAS titrimetric method was added in an attempt to distinguish between bromine and chlorine residuals.

Cooling water samples were collected for the determinations of the water quality parameters listed in Tables 4, 6, and 8. At the COND-IN triplicate 1-liter grab samples were taken before, during, and after chlorination, both from a condenser being chlorinated and from one that was not. Samples were taken at the outfalls during chlorination. A small excess of sodium arsenite was added to all samples taken during chlorination to destroy oxidant residuals. No interference from this procedure was found in any of the analytical methods but there was some evidence that the sodium arsenite did not always react instantaneously with the oxidant residual. This would probably result in lower concentrations of NH_3-N and organic nitrogen in those samples taken during chlorination.

Decay and Receiving Water Studies

Decay studies were conducted on chlorinated cooling water collected at the outfalls. Two 8-liter (2.1 gal) containers lined with polyethylene bags were filled with cooling water. One container was covered to exclude sunlight. No effort was made to keep temperatures constant. Oxidant residuals were determined by the amperometric titration method in both containers over a period of approximately 60 min.

Total oxidant residuals were determined in receiving waters by forward amperometric titrations at all plants except Moss Landing where samples were taken for later titration using the back titration method for free oxidant residual. This was necessary because of the turbulence and wave action at the outfall which caused the micrometer needle of the titrator to vibrate and made the end-point very difficult to read. Receiving water samples were generally taken at the surface although some samples were taken at depths of

1, 2, and 3m (3.3, 6.6, and 9.9 ft). Sampling point locations were determined by reference to features on shore and in some cases by a rope attached to the outfall structure.

ANALYTICAL METHODS AND EQUIPMENT

Oxidant Residual Measurement

Amperometric Titration--

Oxidant residuals were determined amperometrically using Fischer and Porter (Model 17T1010) portable titrators. Total oxidant residuals (TOR) were determined by a direct titration according to Standard Methods (7). TOR could be determined in approximately 1.5 min by applying some suggestions made by Manabe (8). These included the use of a graduated cylinder modified to measure a 200 mℓ sample quickly and the addition of up to 90% of the titrant before turning on the stirrer. The back titration procedure described by White (9) for the determination of free oxidant residual (FOR) was adopted because of an unstable end-point experienced during a direct titration. The term "oxidant residual" has been used rather than "chlorine residual" because the amperometric method measures bromine and iodine residuals in addition to chlorine residuals.

DPD-FAS Titrimetric Method--

The DPD-FAS titrimetric method of Palin (10,11,12) was used to distinguish chlorine and bromine residuals. Three separate titrations give: (A) free chlorine plus free and combined bromine; (B) combined chlorine; (C) free and combined bromine. The separate determination of free and combined bromine is not possible. Some anomalous results were obtained using this method in some of the saline waters.

Water Quality Measurement

Organic nitrogen, chloride, bromide, and suspended solids were all determined according to Standard Methods (7). Ammonia-nitrogen was determined by the phenolhypochlorite method of Solórzano (13). This method was found to be well suited for fresh, marine, and estuarine waters by Zadorojny *et al.*(14).

SECTION 3

RESULTS

IN-PLANT STUDIES

Persistence and decay of oxidant residuals at the outfalls and in the receiving waters can best be explained after the nature and disappearance of the residual inside the plants are understood. The in-plant studies were conducted to establish the nature of the oxidant residual and to gain an understanding of the demands in the cooling water systems at each of the power plants. Each plant was studied separately because of variations in water quality, chlorine dosage, frequency and duration of chlorination, and flow time through the system.

In-plant studies were conducted over a period of one year to be inclusive of varying water quality conditions. Results at each of the four plants studied are presented in Appendix 1 (Figures 20 to 35). The graphs show the temporal variation of oxidant residual during a chlorination cycle. Also shown is the chlorine dose calculated on the basis of the chlorine injection rate determined by power plant personnel and the cooling water flow rate. The calculated dose may not be precise because the chlorine injection rate was difficult to read accurately and the only value usually known for the cooling water flow rate was the original design value.

Contra Costa Power Plant

The results of the in-plant field studies conducted at the Contra Costa Power Plant are summarized in Table 3. Water quality and tidal data corresponding to most of these studies are presented in Table 4.

A combined residual of from 0.10 to 0.40 mg Cl_2/ℓ formed by the time the cooling water reached the COND-IN, (approximately 1.2 min of flow time) and generally remained unchanged at the outfall when the dilution effect was taken into account. It appeared that the FOR which disappeared accounted for most of the loss of residual between the COND-IN and the outfall.

The DPD-FAS results for the study of 14 September 1976 indicated a combined chlorine residual of 0.10 mg/ℓ at the COND-IN and 0.03 mg/ℓ at the outfall, both of which compare favorably with the amperometric titration results. The FOR of 0.20 mg Cl_2/ℓ determined amperometrically titrates as bromine residual by the DPD-FAS method since titration "A" equals titration "C".

Cooling water at Contra Costa varied from 0.3% to 6.1% seawater. Most of the water quality data show the effects of tidal changes. The addition of

TABLE 3. SUMMARY OF FIELD STUDY RESULTS AT CONTRA COSTA POWER PLANT UNITS 6 AND 7

DATE	Cl_2 DOSE CALCULATED	CONDENSER-INLET					OUTFALL MANHOLE†				
		AMP. TIT.		DPD-FAS*			AMP. TIT.		DPD-FAS*		
		TOR	FOR	A	B	C	TOR	FOR	A	B	C
	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$
20 Jan 76	1.6	0.75	0.45	--	--	--	0.18	0.03	--	--	--
10 Feb 76	1.6	0.50	0.10	--	--	--	0.23	0.00	--	--	--
16 Jun 76	1.2	0.55	0.36	--	--	--	0.18	0.08	--	--	--
14 Sep 76	1.3	0.30	0.20	0.20	0.10	0.20	0.04	0.00	0.00	0.03	0.00

*Results of three titrations are: A = Free chlorine plus bromine residuals.
B = Combined chlorine residuals
C = Bromine residuals

†Chlorinated cooling water flow was diluted with an approximately equal volume of unchlorinated water immediately after the condenser.

TABLE 4. WATER QUALITY AND TIDAL DATA AT THE CONTRA COSTA POWER PLANT

DATE/SAMPLE	NH_3-N mg/ℓ	Org-N mg/ℓ	Cl^- mg/ℓ	Br^- mg/ℓ	SUSP. SOLIDS mg/ℓ	pH	TIME OF STUDY	TIDAL DATA TIME	TIDAL DATA ELEVATION, ft§
20 Jan 1976									
#11 COND-IN DUR	0.04*	0.13	50	--	22	--	0930-1200	Hi 0602	+3.9
#14 COND-IN DUR	--	--	50	--	19	--		Lo 1213	+1.0
10 Feb 1976									
#13 COND-IN BEF	0.11*	0.29	563	1.2	42	--	0930-1120	Hi 1039	+4.0
#13 COND-IN DUR	0.09*	0.21	648	1.6	30	--		Lo 1841	+0.2
#13 COND-IN AFT	0.10*	0.20	901	1.9	35	--			
16 Jun 1976									
#13 COND-IN BEF	0.091	0.42	1180	3.9	111	7.5-	1010-1100	Hi 0646	+3.8
#13 COND-IN DUR(+)†	0.066	0.40	1019	3.6	118	7.7		Lo 1415	-0.2
#13 COND-IN DUR(-)‡	0.078	0.43	--	3.5	128	--			
7 OUT DUR	0.082	0.41	--	3.4	114	--			
#13 COND-IN AFT	0.078	0.36	746	2.8	88	--			
14 Sept 1976									
#11 COND-IN BEF	--	0.33	1032	3.9	34	7.7-	1030-1250	Hi 0835	+3.0
#12 COND-IN DUR(+)†	0.019	0.31	--	--	37	8.0		Lo 1403	+1.4
#11 COND-IN DUR(-)‡	0.012	0.33	913	3.5	34	--			
6 OUT DUR	0.009	0.34	--	--	32	--			
#13 COND-IN AFT	0.017	0.32	761	3.4	41	--			

*Determined by nesslerization.
†Samples taken during chlorination cycle from the condenser being chlorinated.
‡Samples taken during chlorination cycle from a condenser not being chlorinated.
§Ft above datum at Golden Gate Bridge.

chlorine generally caused a decrease in ammonia-nitrogen concentrations but this was more evident at the other power plants. Compared with earlier studies the much lower combined residual detected on 14 September 1976 is explained by the very low NH_3-N concentration.

Hunters Point and Potrero Power Plants

The results of the in-plant studies conducted at the Hunters Point and Potrero Power Plants are summarized in Table 5. Water quality and tidal data corresponding to these studies are presented as Table 6.

In general FOR equalled TOR both at the COND-IN and at the outfall. An exception was the study of 17 May 1976 which detected a combined residual at the outfall of 0.13 mg Cl_2/ℓ which had formed during the approximately 0.9 min of flow time from the COND-IN.

The DPD-FAS results for the study of 26 August 1976 at Hunters Point revealed a small combined chlorine residual at the COND-IN which the amperometric method failed to detect. The DPD results at the COND-IN are difficult to explain since titration C should never be greater than titration A. At the outfall a total residual of 0.45 mg Cl_2/ℓ was identified as bromine residual by the DPD-FAS method.

A TOR of 1.0 mg Cl_2/ℓ was desired at the COND-IN for the studies of 23 February 1976 and 4 March 1976 at the Potrero Power Plant. This criterion was lowered to 0.5 mg/ℓ and was the criterion during the studies on the 15th and 17th of October 1976. The studies of 4 March 1976 and 15 October 1976 revealed essentially no loss of oxidant residual between the COND-IN and outfall manhole which corresponded to a flow time of approximately 0.4 min.

Cooling water at Hunters Point and Potrero varied from 79% to 96% seawater. Ammonia-nitrogen concentrations determined on samples collected at the COND-IN decreased by up to 0.091 mg/ℓ during chlorination. A decrease in organic nitrogen was also evident during chlorination.

Moss Landing Power Plant

The results of the in-plant studies at the Moss Landing Power Plant are summarized in Table 7. Water quality and tidal data are presented in Table 8.

The results generally indicate much higher oxidant residuals at the COND-IN than the 1.0 mg/ℓ desired by the plant chemist. Measurements by the amperometric and DPD-FAS methods were often on the order of two times the value determined by the plant chemist during the OT method.

At the COND-IN, FOR was generally greater than or equal to TOR. Since FOR can never be greater than TOR, an error (probably in the TOR measurement) was indicated. Approximately 1 min was required to measure out a 200 mℓ sample, transfer it to the titration jar, add the KI and pH 4 buffer, and perform the TOR titration. During this time the oxidant residual was reacting with species in the water and decaying. On the other hand, the back titration method for FOR fixes the concentration as soon as the sample

TABLE 5. SUMMARY OF FIELD STUDY RESULTS AT THE HUNTERS POINT POWER PLANT (UNIT 4) AND POTRERO POWER PLANT (UNIT 3)

DATE	Cl_2 DOSE CALCULATED	CONDENSER-INLET					OUTFALL MANHOLE†				
		AMP. TIT.		DPD-FAS*			AMP. TIT.		DPD-FAS*		
		TOR	FOR	A	B	C	TOR	FOR	A	B	C
	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$
Hunters Pt.											
16 Dec 76	1.6	0.85	--	--	--	--	0.50	--	--	--	--
17 May 76	1.6	0.72	0.72	--	--	--	0.50	0.37	--	--	--
26 Aug 76	2.5	1.00	1.00	0.60	0.10	0.90	0.70	0.70	0.45	0.00	0.45
19 Oct 76‡	1.2	0.65	0.65	--	--	--	0.24	0.24	--	--	--
Potrero											
23 Feb 76	2.0	1.3-1.5	--	--	--	--	0.5-0.6	--	--	--	--
4 Mar 76	1.6	0.8-1.0	--	--	--	--	0.4-0.5	--	--	--	--
15 Oct 76	0.9	0.73	--	--	--	--	0.35	--	--	--	--
27 Oct 76	0.9	0.73	--	--	--	--	0.28	--	--	--	--

*Results of three titrations are: A = Free chlorine plus bromine residuals.
B = Combined chlorine residual.
C = Bromine Residuals.

†Hunters Point - the cooling water flows through both condensers of Unit 4 and are chlorinated simultan.
Potrero - Chlorinated cooling water was diluted with an approximately equal volume of unchlorinated water immediately after the condensers.

‡Cooling water flows through the condensers were chlorinated separately for this study.

TABLE 6. WATER QUALITY AND TIDAL DATA AT THE HUNTERS POINT AND POTRERO POWER PLANTS

DATE/SAMPLE	NH_3-N	Org-N	Cl^-	Br-	S.S.	pH	TIME OF STUDY	TIDAL DATA	
	mg/ℓ	mg/ℓ	g/ℓ	mg/ℓ	mg/ℓ			TIME	ELEVATION ft
Hunters Point									
16 Dec 75									
COND-IN DUR	0.06*	0.33	15.4	--	14	--	1100-1145		
17 May 76									
COND-IN BEF	0.134	0.18	18.2	71	27	7.0	1040-1120	Hi 1655	+5.8
COND-IN DUR	0.047	0.08	17.7	70	19	--		Lo 0959	-1.1
OUT DUR	0.036	0.03	--	--	19	--			
COND-IN AFT	0.119	0.14	17.9	70	21	--			
26 Aug 76									
COND-IN BEF	0.128	0.34	18.7	72	31	7.5	1040-1120	Hi 1422	+7.1
COND-IN DUR	0.037	0.28	--	--	28	--		Lo 0813	+1.6
OUT DUR	0.024	0.28	--	--	28	--			
COND-IN AFT	0.140	0.36	18.4	73	27	--			
Potrero									
23 Feb 76									
N. COND-IN BEF	0.055	0.27	16.8	67	13	--	2100-2215	Hi 2026	+4.8
N. COND-IN DUR	0.000	0.20	16.5	71	11	--		Lo 2509	+2.7
OUT DUR	0.032	0.21	16.5	70	12	--			
N. COND-IN AFT	0.075	0.26	16.4	71	10	--			
4 Mar 76									
N COND-IN BEF	0.118	0.20	16.7	63	18	--	2100-2215	Hi 2625	+5.7
N COND-IN DUR	0.059	0.16	16.8	64	15	--		Lo 2000	+1.6
OUT DUR	0.077	0.21	--	--	17	--			
S COND-IN AFT	0.104	0.17	16.8	66	20	--			

*Determined by nesslerization.
†Ft above datum at Golden Gate Bridge.

TABLE 7. SUMMARY OF FIELD STUDY RESULTS AT THE MOSS LANDING POWER PLANT UNITS 6 AND 7

DATE	Cl_2 DOSE CALCULATED	CONDENSER-INLET					ISE SAMPLING POINT†				
		AMP. TIT.		DPD-FAS*			AMP. TIT.		DPD-FAS*		
		TOR	FOR	A	B	C	TOR	FOR	A	B	C
	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$	$mgCl_2/\ell$
12 Apr 76	2.2	1.35-1.65	--	--	--	--	0.15-0.18	--	--	--	--
19 Apr 76	2.2	1.45-2.10	--	--	--	--	0.23-0.31	--	--	--	--
14 Jul 76	2.1	1.40-1.80	1.60-1.90	1.70-2.00	0.00	1.80-2.20	0.15-0.20	0.10-0.14	--	--	--
22 Jul 76	2.1	1.30-2.10	1.40-2.20	1.25-1.65	0.00	1.60-2.00	--	--	--	--	--
5 Aug 76	1.3	0.80-1.20	0.90-1.35	0.50-0.80	0.05	0.70-1.20	0.05-0.15	0.05-0.10	0.08-0.11	0.05-0.10	0.03-0.05
23 Sep 76	2.1	1.00-1.70	1.00-1.80	1.10-1.70	0.00	1.70-2.20	0.24-0.40	0.30-0.40	--	--	--

*Results of three titrations are: A = Free chlorine plus bromine residual.
B = Combined chlorine residual.
C = Bromine residual.

†Chlorinated cooling water was diluted with an approximately equal volume of unchlorinated water immediately after the condensers.

TABLE 8. WATER QUALITY AND TIDAL DATA AT THE MOSS LANDING POWER PLANT

DATE/SAMPLE	NH_3-N	Org-N	Cl^-	Br^-	SUSP. SOLIDS	pH	TIME OF STUDY	TIDAL DATA	
	mg/ℓ	mg/ℓ	g/ℓ	mg/ℓ	mg/ℓ			TIME	ELEVATION ft
12 Apr 76									
7-1 COND-IN BEF	0.096	0.20	19.0	78	19	7.9-	1240-	Hi 0838	+4.7
7-2 COND-IN DUR(+)*	0.021	0.09	18.7	82	22	8.0	1330	Lo 1438	+0.5
7-1 COND-IN DUR(-)†	0.114	0.19	18.8	81	21				
7-2 COND-IN AFT	0.137	0.25	18.5	82	21				
19 Apr 76									
7-1 COND-IN BEF	0.058	0.16	18.9	68	31	7.8	1300-	Hi 1533	+4.1
7-2 COND-IN DUR(+)*	0.005	0.08	19.0	70	14		1350	Lo 0840	-0.6
7-1 COND-IN DUR(-)†	0.033	0.12	18.8	67	15				
7 ISE DUR	0.016	0.10			19				
7-2 COND-IN AFT	0.037	0.04	19.1	74	20				
14 Jul 76									
6-1 COND-IN BEF	0.046	0.19	18.6	82	12	8.1-	1300-	Hi 1403	+4.8
6-2 COND-IN DUR(+)*	0.000	0.19	--	--	14	8.2	1400	Lo 0720	-0.4
6-1 COND-IN DUR(-)†	0.038	0.19	--	--	8				
6 ISE DUR	0.010	0.19	--	--	12				
6-1 COND-IN AFT	0.047	0.19	19.1	80	8				
22 Jul 76									
6-1 COND-IN BEF	0.072	0.30	18.8	78	15	8.0-	1300-	Hi 0908	+3.5
6-2 COND-IN DUR(+)*	0.010	0.19	--	--	9	8.1	1350	Lo 1327	+2.8
6-1 COND-IN DUR(-)†	0.120	0.30	--	--	11				
6-1 COND-IN AFT	0.093	0.26	18.9	74	10				

(continued)

TABLE 8 (continued)

DATE/SAMPLE	NH_3-N	Org-N	Cl^-	Br^-	SUSP. SOLIDS	pH	TIME OF STUDY	TIDAL DATA	
								TIME	ELEVATION ft ‡
	mg/ℓ	mg/ℓ	g/ℓ	mg/ℓ	mg/ℓ				
5 Aug 76									
6-1 COND-IN BEF	0.074	0.22	18.8	73	23	8.2-	1300-	Hi 0826	+3.8
6-1 COND-IN DUR(+)*	0.016	0.17	--	--	18	8.3	1400	Lo 1307	+2.7
6-2 COND-IN DUR(-)†	0.072	0.21	--	--	18				
6 ISE DUR	0.045	0.17	--	--	16				
6-1 COND-IN AFT	0.074	0.23	19.1	70	18				
23 Sept 76									
6-1 COND-IN BEF	0.052	0.19	18.7	70	3	8.9	1300-	Hi 1044	+5.4
6-1 COND-IN DUR(+)*	0.045	0.25	--	--	5		1350	Lo 1656	+0.3
6-2 COND-IN DUR(-)†	0.071	0.22	--	--	4				
6 ISE DUR	0.017	0.16	--	--	2				
6-1 COND-IN AFT	0.103	0.30	18.6	67	4				

*Samples taken during chlorination cycle from the condenser being chlorinated.

†Samples taken during chlorination cycle but from a condenser not being chlorinated.

‡Ft above datum at Golden Gate Bridge.

is mixed with excess phenylarsine oxide and pH 7 buffer. Another contributing factor to this result was the flashing off of iodine during stirring in the forward titration for TOR.

The DPD-FAS results indicated little or no combined chlorine residual at the COND-IN. Some combined chlorine was indicated at ISE both by the amperometric and DPD-FAS methods. Most of the DPD-FAS results must be regarded with suspicion because of the discrepancy between titrations A and C.

Cooling water at Moss Landing varied from 95% to 99% seawater. Ammonia-nitrogen concentrations determined on samples collected at the COND-IN decreased by up to 0.075 mg/ℓ due to chlorination. A decrease of organic nitrogen during chlorination was observed in 4 of the 6 studies.

Summary

The DPD-FAS titrimetric method was added to the field studies to gain a better understanding of the nature of the oxidant residual at the power plants. The results of two studies that were conducted in the laboratory comparing this method with the amperometric method are presented in Figure 7. Chlorine (sodium hypochlorite) was added to 4-liter samples of San Francisco Bay water and oxidant residuals were determined for a period of 40 min. A good correlation between FOR determined amperometrically and titration A of the DPD-FAS method was obtained. TOR determined by the amperometric method was equal to or slightly less than TOR calculated from the DPD-FAS results (titration A plus B). The discrepancy between amperometric and DPD TOR data appeared to result from the underestimation of combined chlorine residual by the amperometric method. Results of titration C indicated that most of the FOR was bromine residual.

Table 9 summarizes the disappearance of oxidant residual observed for all the in-plant studies. Loss of residual is expressed as a percentage of the chlorine dose. The table does not included the decrease of oxidant residual due to dilution immediately after the condensers. The measured TOR at the outfalls has been doubled before the percentage loss was calculated for those plants where such a dilution occurred. Flow times between the sampling points at each plant are indicated. Results at Contra Costa are separated for Units 6 and 7 because of the different flow times from the COND-IN to the outfall.

The table shows that the disappearance of TOR generally depends on the flow time through the system. This is especially evident from the COND-IN to the outfall because of the wide variation of flow times that existed. Figure 8 is a graph of the percentage loss of TOR between the COND-IN and the outfall sampling point as a function of flow time.

DECAY AND RECEIVING WATER STUDIES

Decay studies were conducted on the chlorinated cooling water collected at the outfalls to determine the approximate life of oxidant residuals in the receiving waters. Oxidant residuals were measured at various locations in

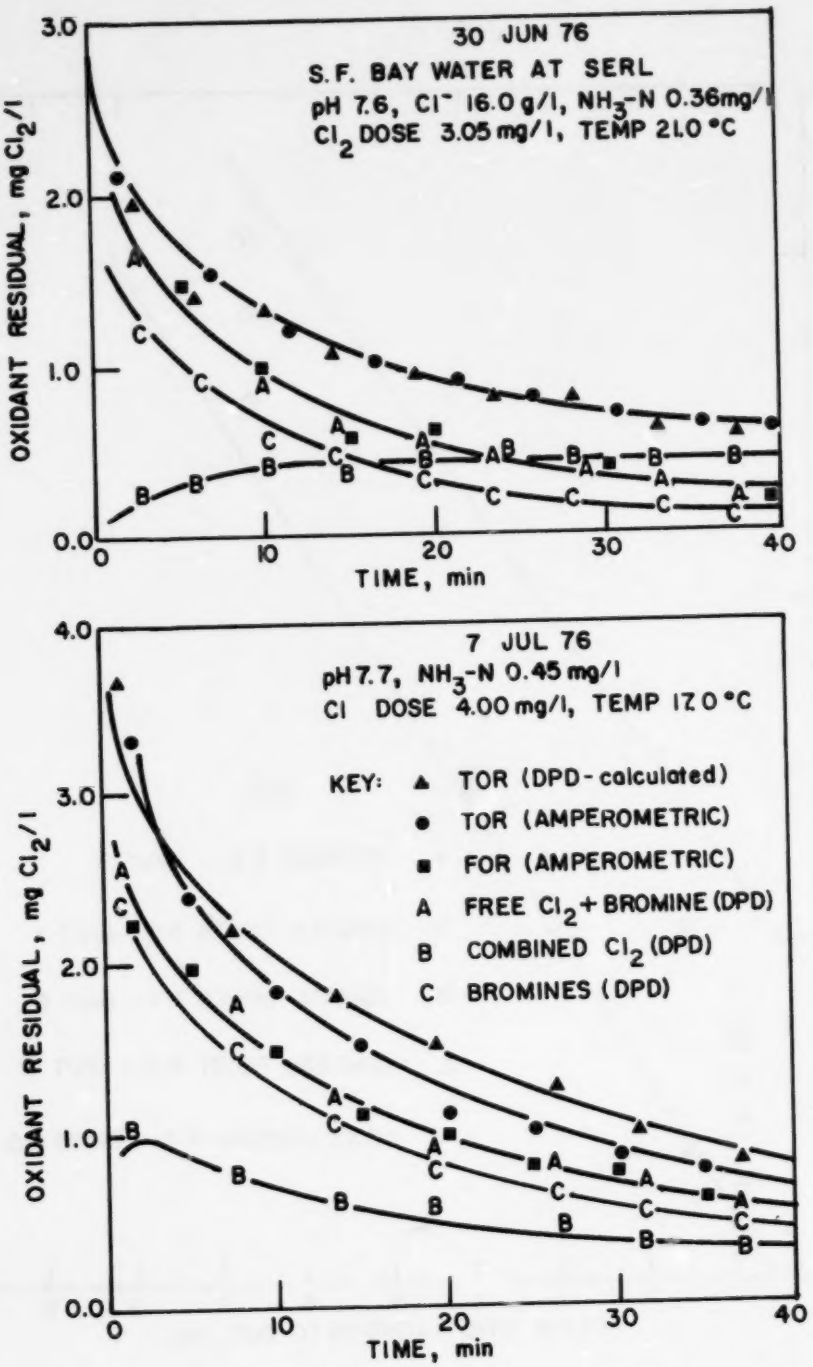
30 JUN 76
S.F. BAY WATER AT SERL
pH 7.6, Cl⁻ 16.0 g/l, NH3-N 0.36mg/l
Cl2 DOSE 3.05 mg/l, TEMP 21.0 °C
OXIDANT RESIDUAL, mg Cl2/l
TIME, min
7 JUL 76
pH 7.7, NH3-N 0.45 mg/l
Cl DOSE 4.00 mg/l, TEMP 17.0 °C
KEY: ▲ TOR (DPD-calculated)
● TOR (AMPEROMETRIC)
■ FOR (AMPEROMETRIC)
A FREE Cl2 + BROMINE (DPD)
B COMBINED Cl2 (DPD)
C BROMINES (DPD)
OXIDANT RESIDUAL, mg Cl2/l
TIME, min

Figure 7. Laboratory comparison of DPD-FAS titrimetric and amperometric titration methods.

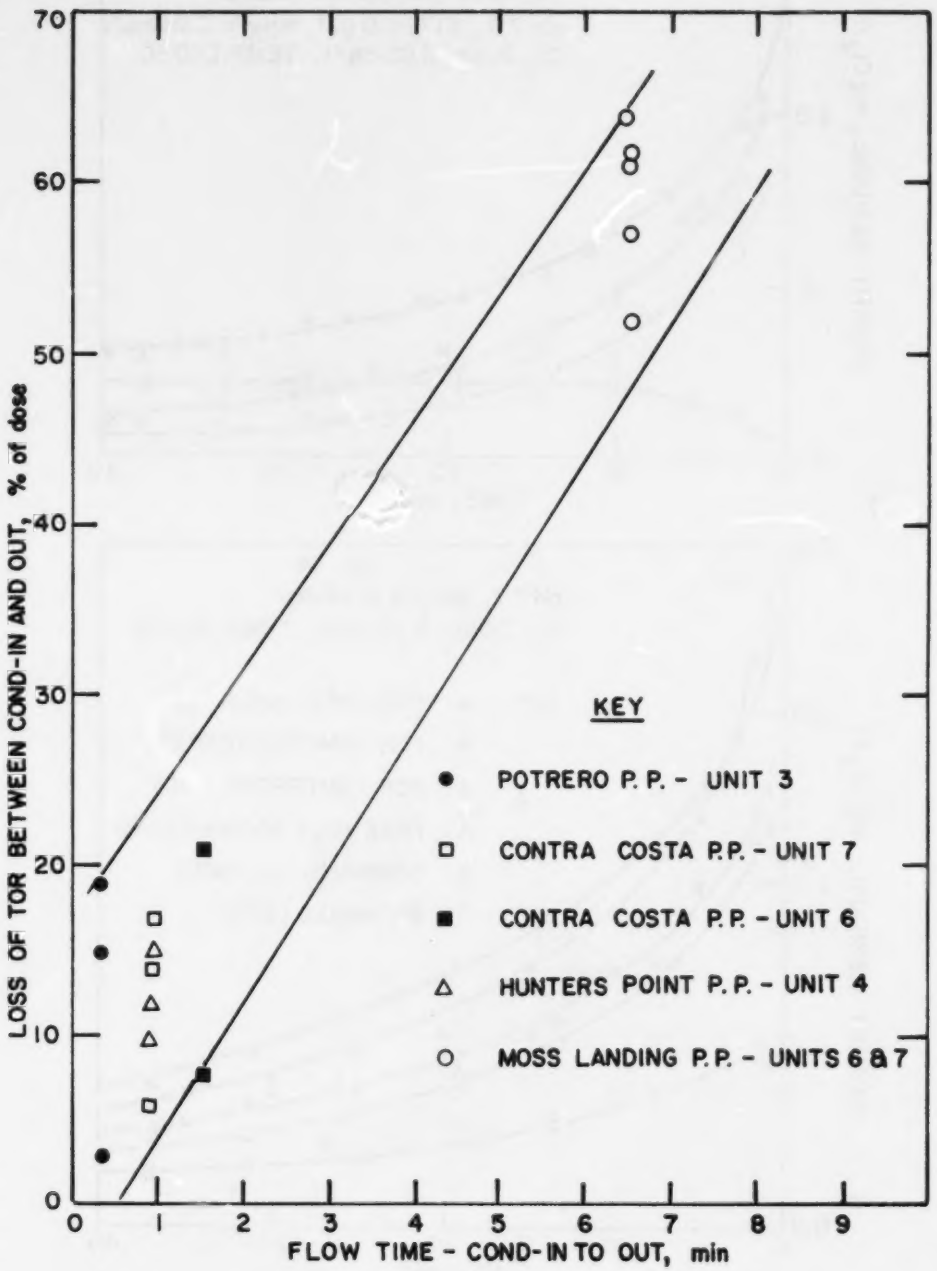

Figure 8. Percentage loss of TOR between the COND-IN and the outfall sampling point for various power plants.

TABLE 9. SUMMARY OF LOSS OF OXIDANT RESIDUAL WITHIN THE POWER PLANT COOLING WATER SYSTEM

POWER PLANT	UNIT	APROXIMATE FLOW TIME (min)			TOR LOSS (%)*		TOR (%)* REMAINING AT OUTFALL†
		INJ PT TO COND-IN	COND-IN TO OUTFALL†	TOTAL	INJ PT TO COND-IN	COND-IN TO OUTFALL†	
Contra Costa	6	1.2	1.5	2.7	55-75	8-21	17-24
	7	1.2	0.9	2.1	54-67	6-17	27-31
Hunters Point	4	1.5	0.9	2.4	44-59	10-34	24-40
Potrero	3	0.9	0.4	1.3	19-44	0-19	54-78
Moss Landing	6,7	0.8	6-7	7-8	10-32	41-64	16-27

*Percent loss does not include that caused by dilution immediately past the condensers.

†ISE at Moss Landing

the receiving waters to determine the extent of the area affected by the power plant discharge during chlorination.

The results of the decay studies conducted at the outfalls are presented in Figures 9-12. The loss of oxidant residual between the point of chlorine injection, the COND-IN, and the outfall are shown. The effect of the 1:1 dilution which occurred between the COND-IN and the outfall sampling point is indicated by a dotted line for all plants except Hunters Point where flows to both condensers were chlorinated simultaneously. Table 10 is a summary of the decay studies. It should be remembered that the results are based on field studies and that no attempt was made to keep temperature constant. In most cases temperature increased in the "light" experiments and decreased in the "dark" experiments.

The results of receiving water studies are presented in Figures 13-17 in the form of isoconcentration lines of TOR at the surface. Surface TOR was always found to be the highest compared to samples taken at various depths. Whenever possible the 0.02, 0.05, and 0.10 mg Cl_2/ℓ isoconcentration lines are shown together with the enclosed surface areas. These areas give an approximation of the regions affected by various levels of TOR. The receiving water studies conducted at Contra Costa, Potrero, and Hunters Point were for a time period greater than the normal chlorination cycles at these plants.

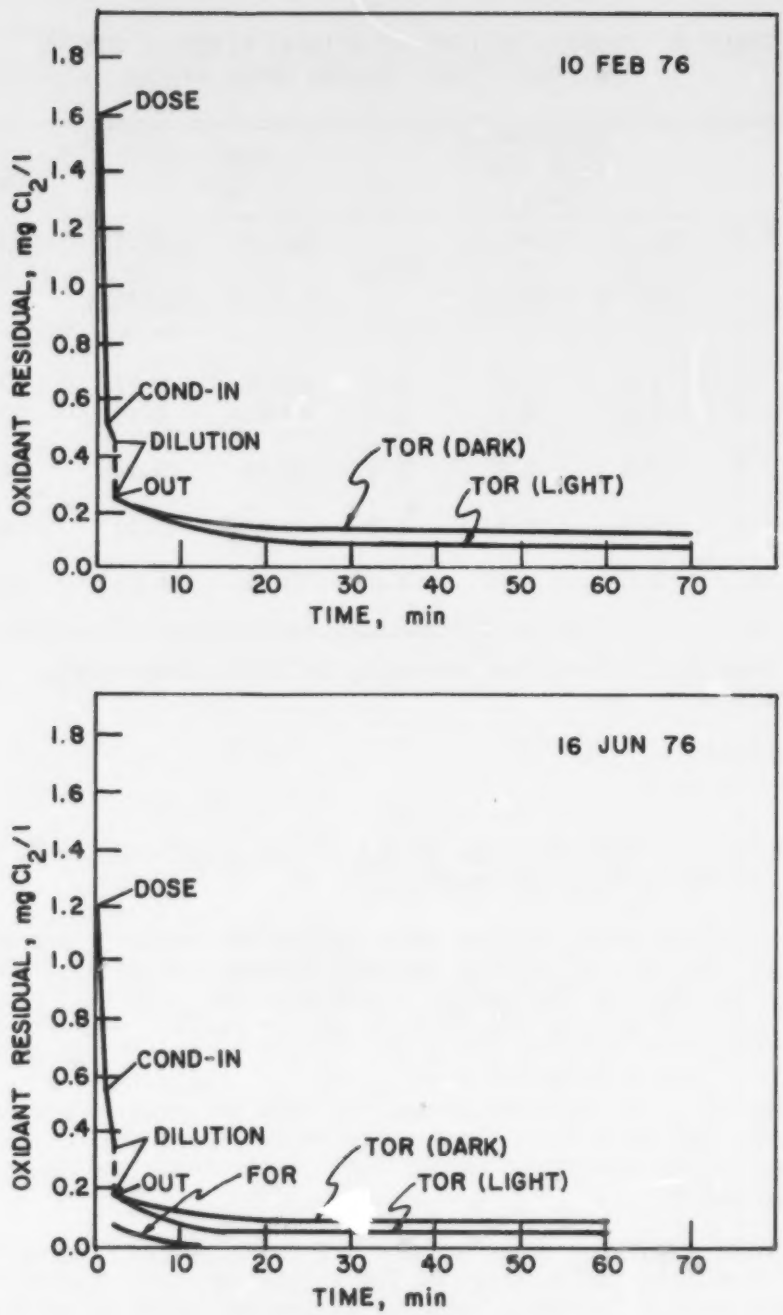

Figure 9. Results of decay studies conducted at the Contra Costa power plant, Units 6 and 7 outfall.

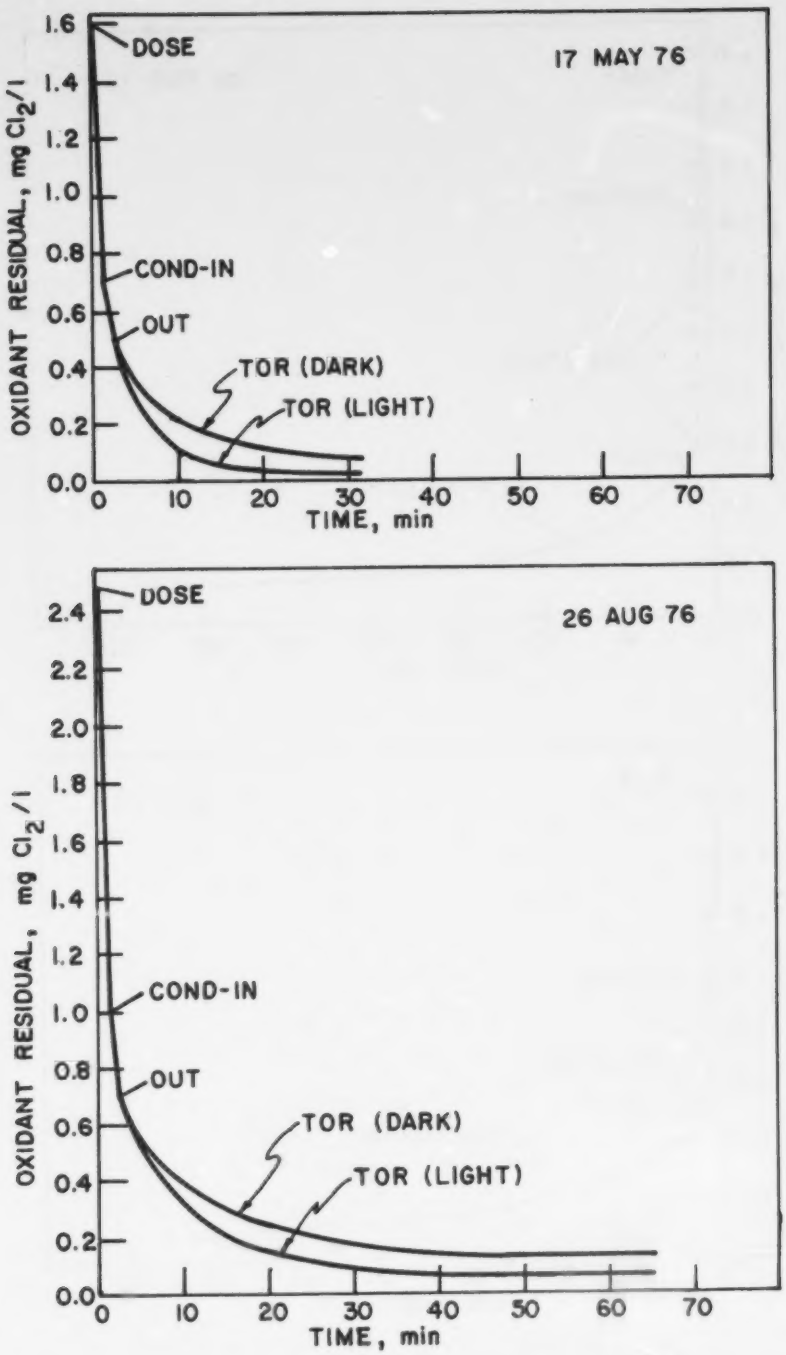

Figure 10. Results of decay studies conducted at the Hunters Point Power Plant, Unit 4 outfall.

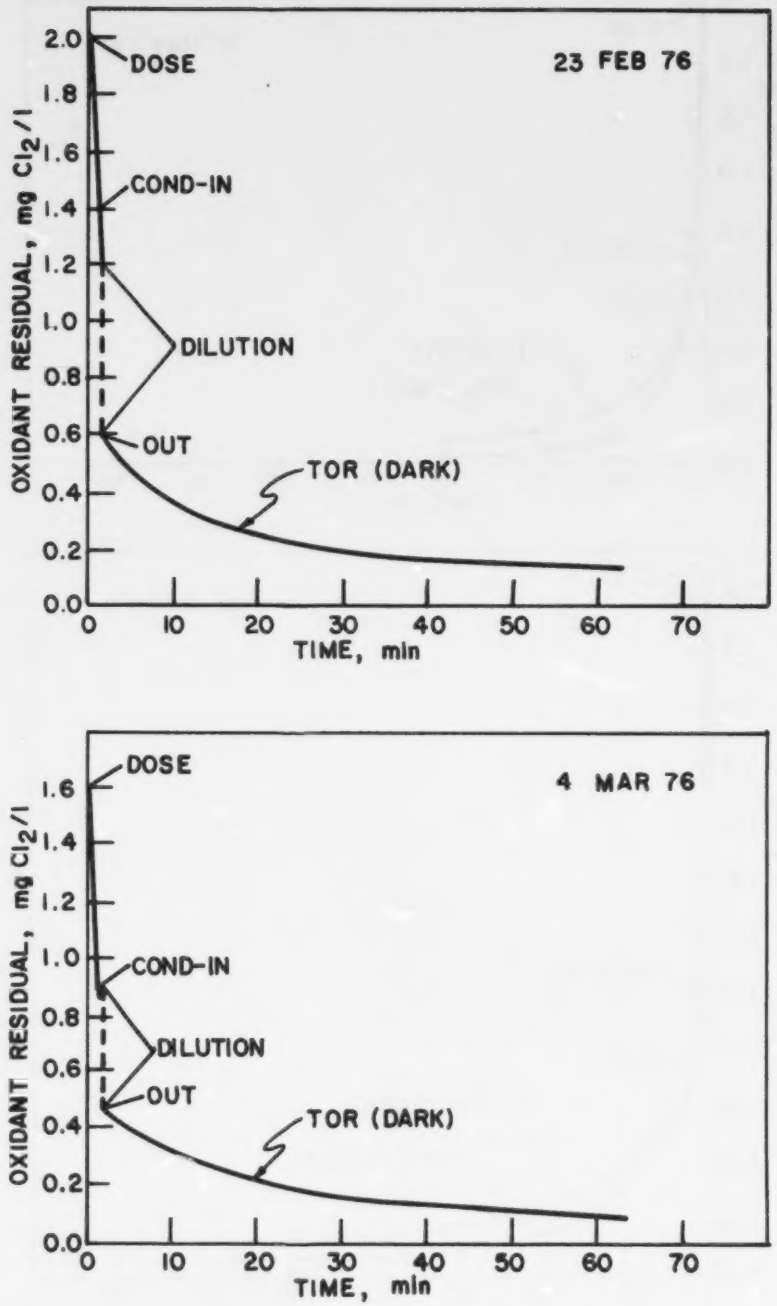

Figure 11. Results of decay studies conducted at the Potrero power plant, Unit 3 outfall.

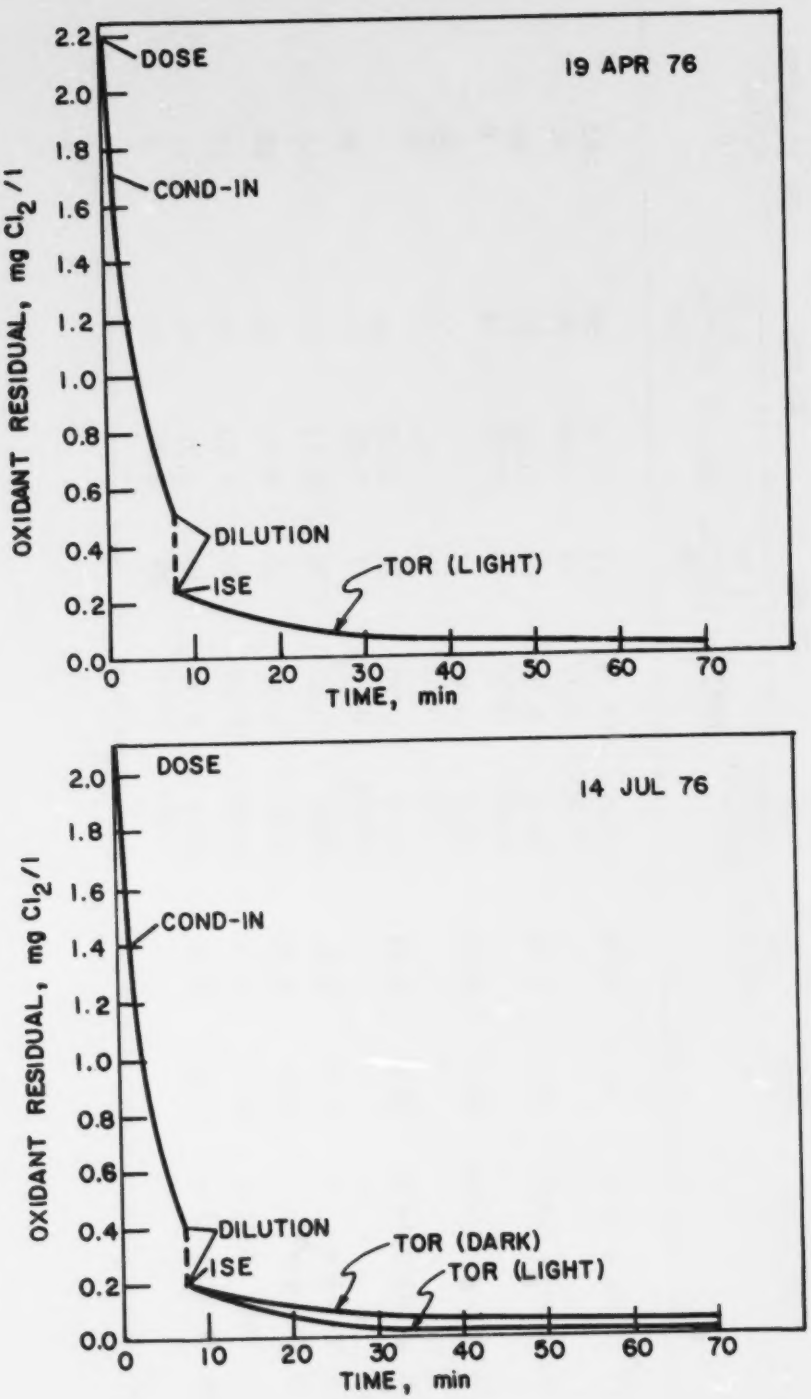

Figure 12. Results of decay studies conducted at the Moss Landing power plant, Units 6 and 7 at ISE.

TABLE 10. SUMMARY OF DECAY STUDIES

DATE	POWER PLANT	INITIAL TEMP °C	INITIAL TOR $mgCl_2/\ell$	"DARK" OR "LIGHT" EXPOSURE	TOR AFTER 30 MIN		TOR AFTER 60 MIN		TIME TO REACH 0.1 $mgCl_2/\ell$ min
					$mgCl_2/\ell$	% OF INITIAL TOR	$mgCl_2/\ell$	% OF INITIAL TOR	
10 Feb 76	Contra Costa	--	0.23	Dark	0.14	61	0.12	52	>90
				Light	0.12	52	0.09	39	45
16 Jun 76	Contra Costa	34.5	0.16	Dark	0.09	56	0.08	50	20
				Light	0.07	44	0.06	38	8
17 May 76	Hunters Point	24.0	0.52	Dark	0.10	17	--	--	30
				Light	0.03	6	--	--	10
26 Aug 76	Hunters Point	30.0	0.72	Dark	0.20	28	0.15	21	
				Light	0.12	17	0.08	11	38
23 Feb 76	Potrero	20.0	0.61	Dark	0.20	33	0.13	21	>90
4 Mar 76	Potrero	20.0	0.43	Dark	0.15	35	0.10	23	60
19 Apr 76	Moss Landing	24.0	0.22	Light	0.08	35	0.03	13	22
14 Jul 76	Moss Landing	27.0	0.20	Dark	0.08	40	0.05	25	16
				Light	0.05	25	0.02	10	8

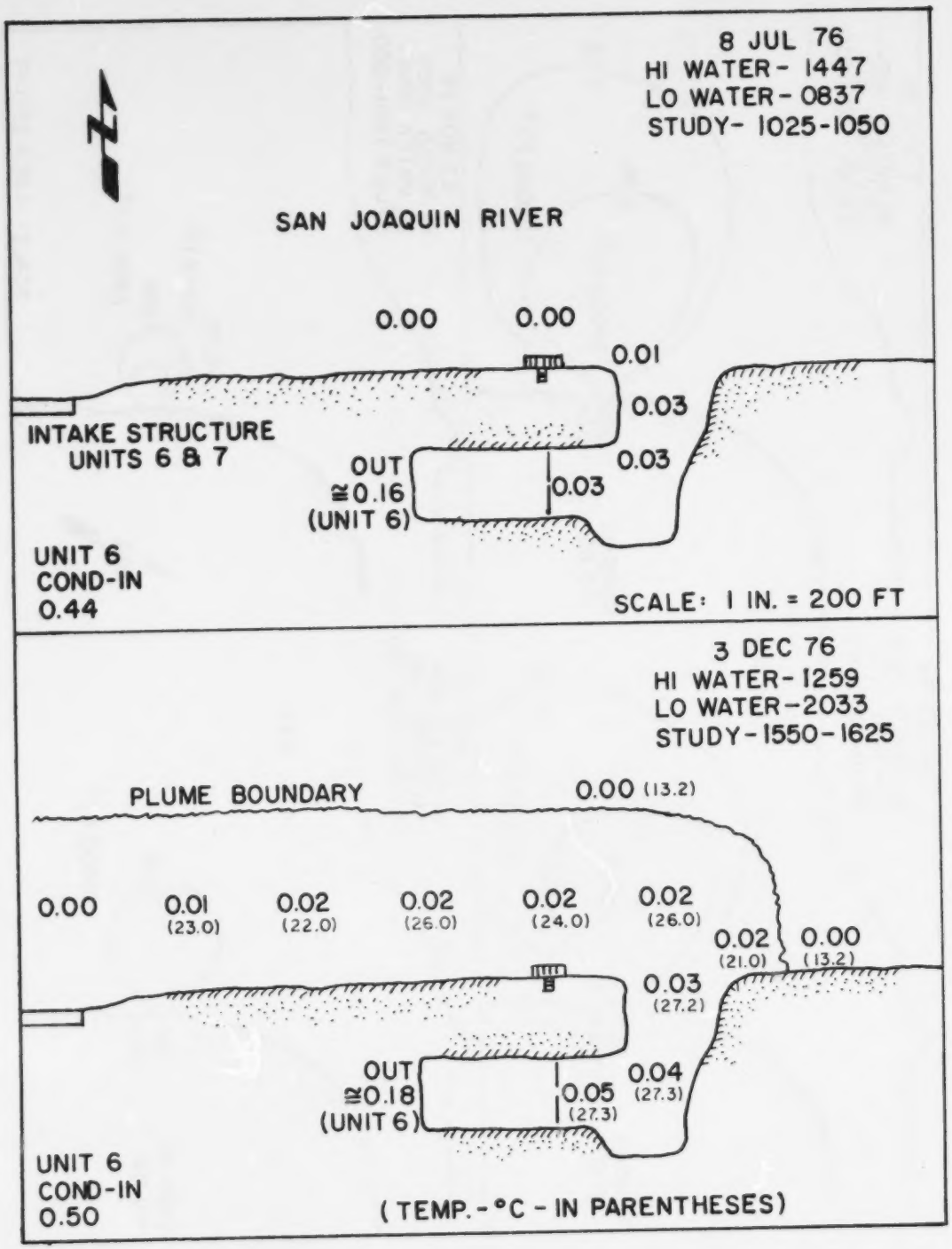

Figure 13. TOR ($mgCl_2/\ell$) at the surface of the receiving water at the Contra Costa power plant, Units 6 and 7.

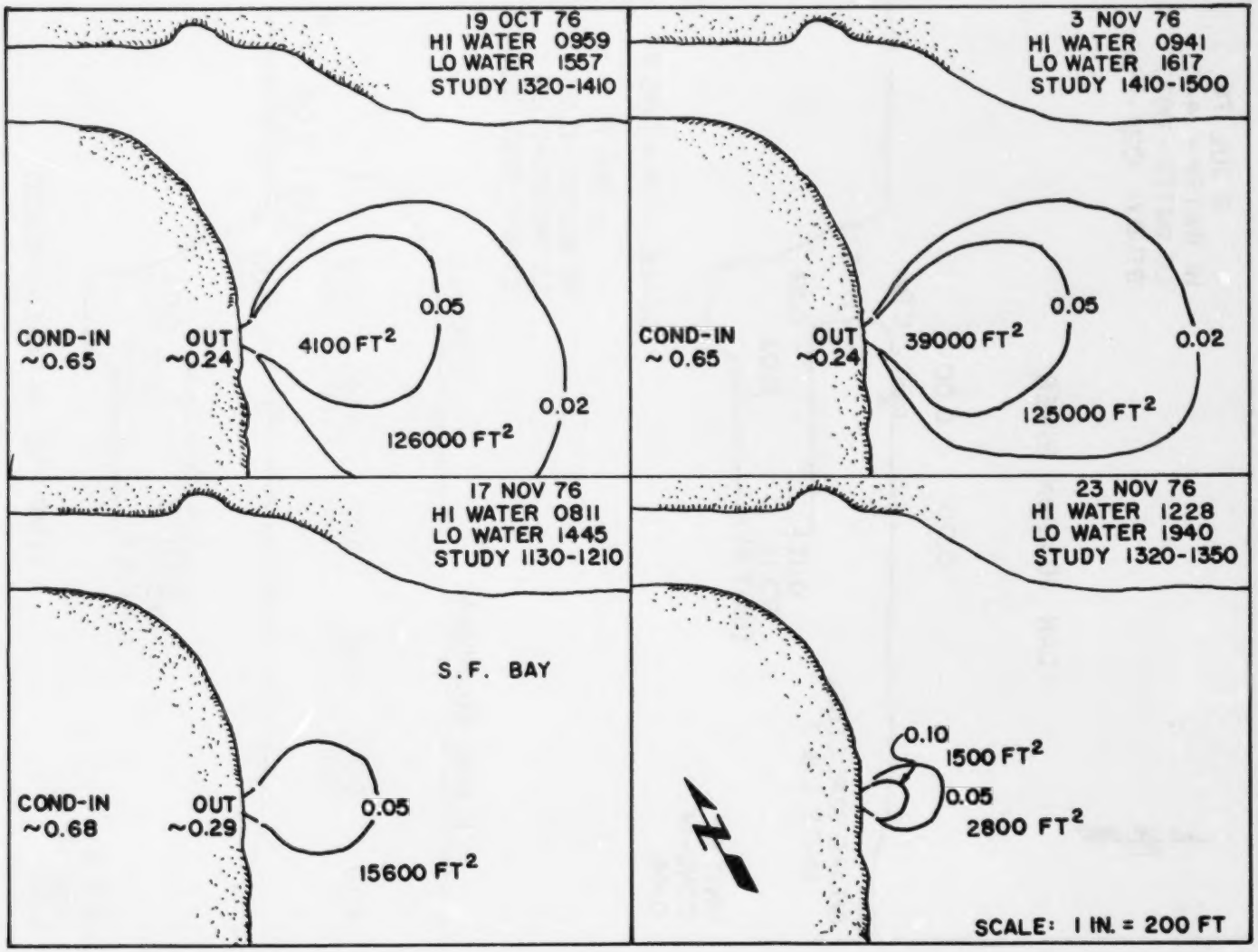

Figure 14. TOR ($mgCl_2/\ell$) at receiving water surface at the Hunters Point Power Plant, Unit 4.

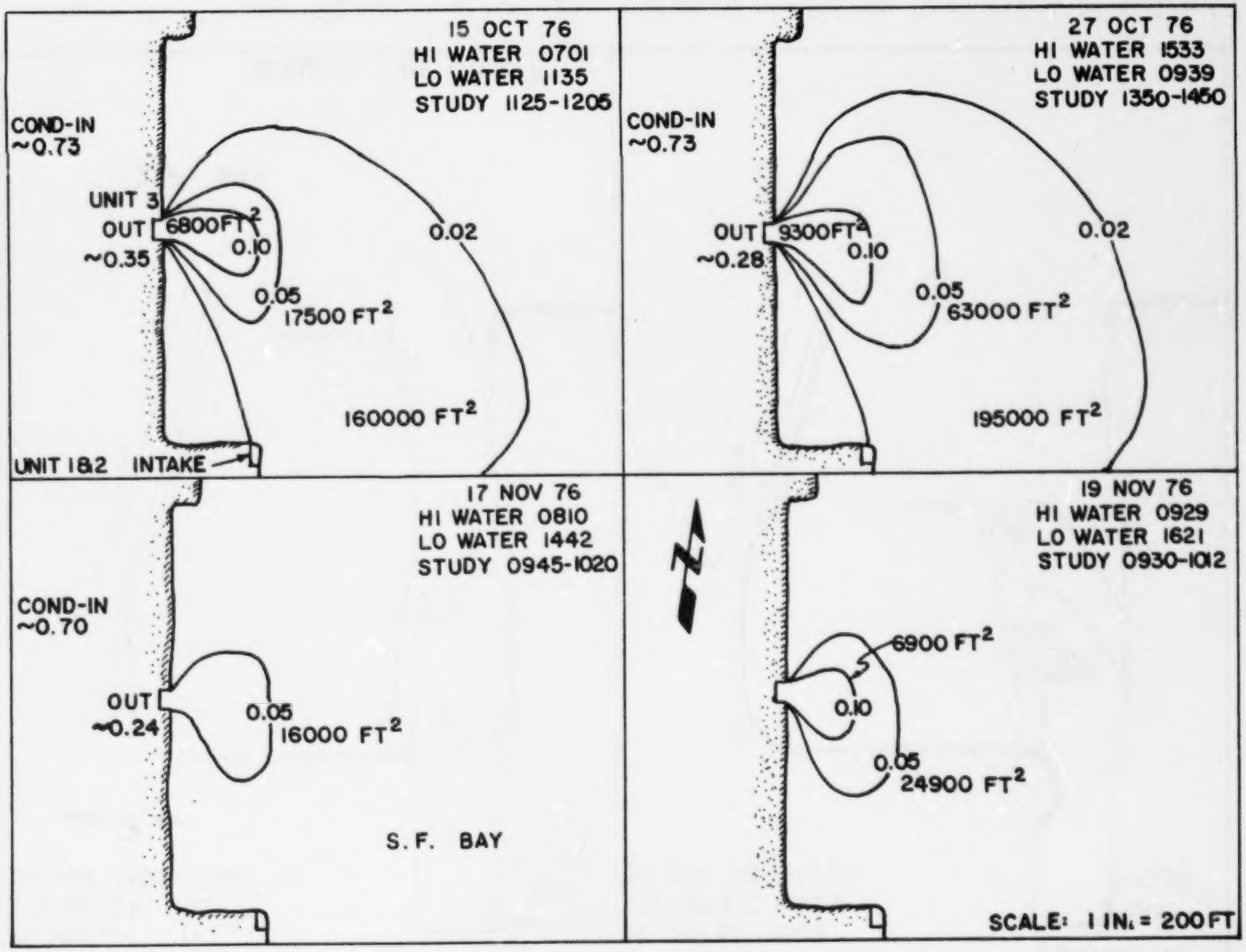

Figure 15. TOR ($mgCl_2/\ell$) at receiving water surface at the Potrero power plant, Unit 3.

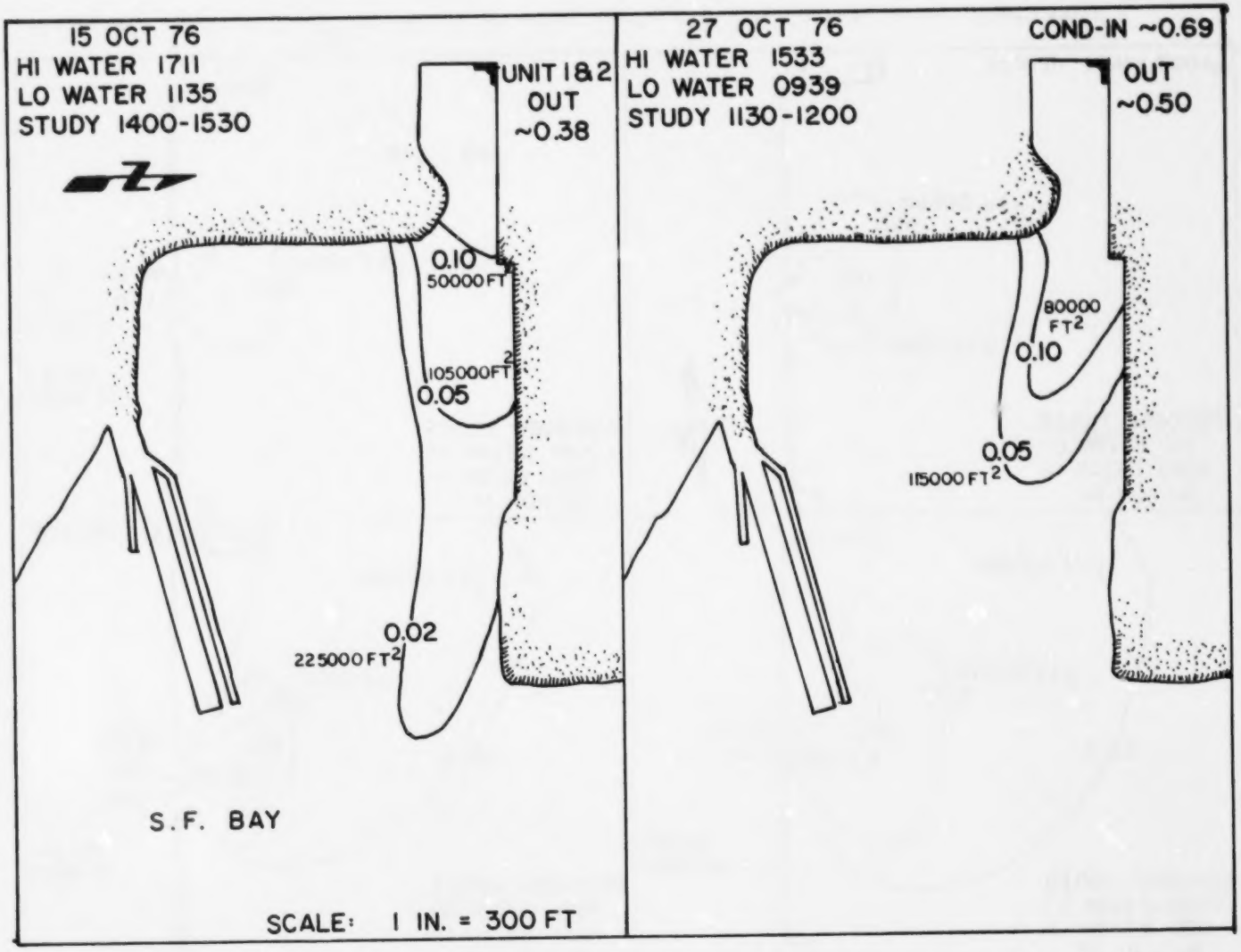

Figure 16. TOR ($mgCl_2/\ell$) at receiving water surface at the Potrero Power Plant, Units 1 and 2.

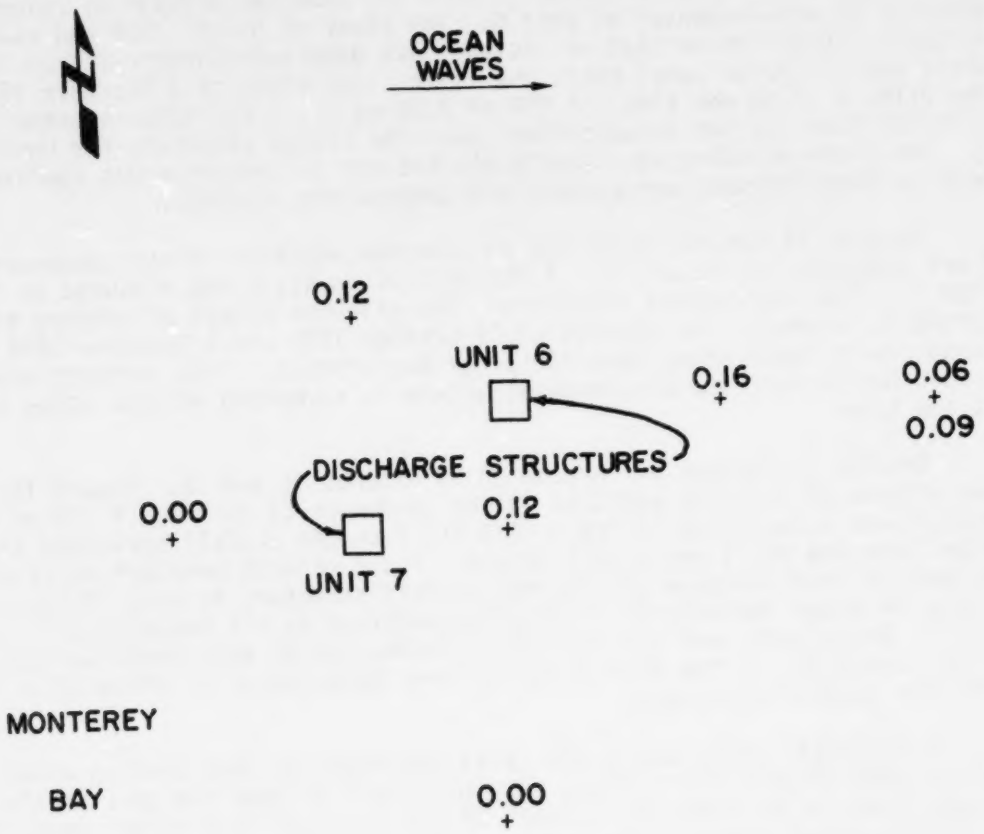

Figure 17. FOR ($mgCl_2/\ell$) at the receiving water surface at the Moss Landing power plant, Unit 6.

The results at Contra Costa (Figure 13) show the effects of chlorine addition to one condenser of Unit 6. The study of 8 July 1976 was conducted during a flood tide so that no residual was detected downstream from the point where the discharge canal meets the river. The study of 3 December 1976 shows the effects of an ebb tide. A TOR of 0.02 mg Cl_2/ℓ was detected some 150m (500 ft) down the San Joaquin River near the intake structure for Units 6 and 7. The plume boundary was clearly visible and its presence was confirmed by both oxidant residual measurement and temperature readings.

Results at Hunters Point due to chlorine addition to one condenser of Unit 4 are presented in Figure 14. A TOR of 0.02 mg Cl_2/ℓ was measured up to 150m (500 ft) from the outfall structure. The dilution effect of varying tidal stages is evident. The studies of 19 October 1976 and 3 November 1976 were conducted at lower tides than the other two studies. Tidal effects are very pronounced because the discharge structure is submerged at high tides but not at low tides.

Results at Potrero are presented in Figures 15 and 16. Figure 15 shows the effects of chlorine addition to one condenser of Unit 3. A TOR of 0.02 $mgCl_2/\ell$ was detected up to 168 m (550 ft) from the outfall structure and is drawn into the No. 1 and 2 Unit intake. Tidal effects were not as evident as at Hunters Point because the Potrero outfall structure is never fully submerged. Figure 16 shows the effects of chlorine addition to all condensers of Units 1 and 2. These units are very old and chlorination of each condenser separately is not possible. A TOR of 0.02 $mgCl_2/\ell$ was detected up to 400 m (1300 ft) from the outfall structure.

A study was conducted in the receiving water at Moss Landing on 23 September 1976 (Figure 17). It was very difficult to keep the boat in the discharge plume in Monterey Bay because of the force of 37.9 m^3/sec (600,000 gpm) of cooling water reaching the surface. It was difficult at times to determine the exact location of the plume because of waves continually moving the boat. A maximum TOR of 0.16 mg Cl_2/ℓ was determined at the surface at a time when the TOR ranged from 1.2 to 1.7 mg/ℓ at the COND-IN and from 0.31 to 0.33 mg/ℓ at ISE.

SECTION 4

DISCUSSION

NATURE OF THE OXIDANT RESIDUAL

The nature of the oxidant residual at each of the power plants is important for understanding the decay and persistence in the receiving waters. None of the methods currently available for the routine measurement of oxidant residuals unequivocally identify the compounds that make up the residual. This is especially true for oxidant residuals in estuarine and marine waters.

When chlorine is added to seawater that is free of amino-nitrogen, bromide (present at a concentration of approximately 70 mg/ℓ) is oxidized to bromine as follows:

$$HOCl + Br^- = HOBr + Cl^-$$

Figure 18 shows the time required (based on reported rate constants) to convert 99% of the chlorine to bromine at a temperature of 25°C and a pH of 8.3 for varying percentages of seawater (15). The reaction proceeds to 99% completion within 10 sec in highly saline water, but very little bromine is formed in water containing less than 3% seawater. A similar oxidation of iodine occurs. Total oxidation of the iodide in seawater to iodine would account for a TOR of 0.035 mg/ℓ as chlorine.

When ammonia-nitrogen is present in seawater, there is a competition between the ammonia and the bromide ion for chlorine. A number of reactions are possible, depending on pH, chlorine dose, concentration of NH_3-N, salinity, and reaction time. The formation of chloramines is generally favored by high NH_3-N, low salinity, high pH, and low chlorine dosage.

Using an equilibrium model, Sugam and Helz (16) suggest that free bromine and bromamines predominate over the chlorine species at salinities above approximately 0.3 g/ℓ with ammonia concentrations "typical" of estuarine and marine waters. The predominant species in seawater containing 0.08 mg NH_3-N/ℓ dosed at 1.0 mgCl_2/ℓ at pH 8.1 were tribromamine (NBr_3) and dibromamine ($NHBr_2$). Equal amounts of monochloramine (NH_2Cl) and HOBr were estimated to exist in a typical seawater of 35 g/ℓ salinity at pH 8 containing 0.12 mg/ℓ NH_2-N dosed at 0.5 mgCl_2/ℓ. The model for 0.3 g/ℓ salinity is very complicated showing both chlorine and bromine compounds with no species in abundance between pH 6 and 8.

Sollo et al. (17) performed studies on the resulting speciation when solutions containing both ammonia and bromide were dosed with chlorine and the

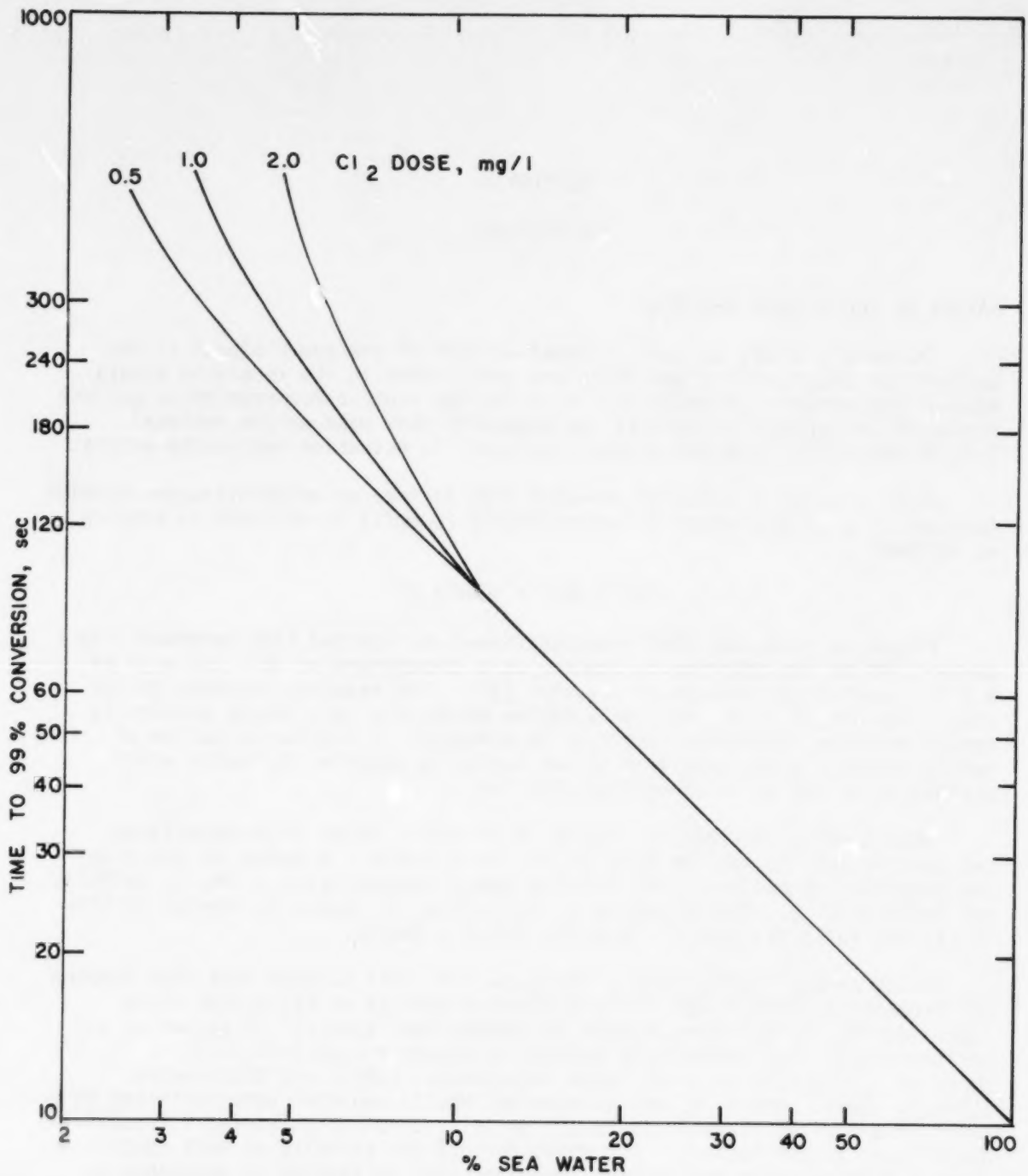

Figure 18. Time required for 99% conversion of free chlorine to HOBr at 25°C and a pH of 8.3[15]

residuals were determined after 2 min. Solutions containing 0.41 mg/ℓ NH_3-N and bromide concentrations of 3 and 25 mg/ℓ dosed at 2 mgCl_2/ℓ are interesting because they most closely model the conditions existing in the cooling waters studied in this investigation. Very little free bromine existed over the entire pH range tested (4.3 to 9.0). At pH 7.4 and 25 mg/ℓ Br^- a total halogen concentration of 2.8 mg Br_2/ℓ was detected which was significantly lower than the 4.5 mg Br_2/ℓ expected. The entire residual was determined to be combined bromine and was believed to be $NHBr_2$ whose instability might explain the lower than expected total halogen residual. At pH 7.4 and 3 mg/ℓ Br^- the entire 4.5 mg Br_2/ℓ total halogen residual was determined to be chlorine residual.

Figure 19 after Johnson and Overby (18) shows the bromine species postulated to be present after 1 to 2 min as a function of both pH and the logarithm of the initial mole ratio of ammonia to bromine. These data suggest that HOBr and NBr_3 would predominate after 1 to 2 min under conditions that exist at the Hunters Point, Potrero, and Moss Landing Power Plants if a total conversion of chlorine to bromine is assumed. $NHBr_2$ would be predominant at somewhat higher ammonia concentrations than were measured at the power plants. At Contra Costa both chlorine and bromine compounds are suggested with prediction of individual species being difficult. It is apparent that both chlorine and bromine residuals generally exist when chlorine is added to estuarine and marine waters. Both the amperometric and DPD-FAS methods were used to determine oxidant residuals. The amperometric titration method for total residual determines all oxidant residuals whether they be chlorine, bromine, or iodine. It is apparent from Figure 11 that the amperometric free residual determination measures both free chlorine and bromine residual. Since the DPD-FAS method does not distinguish between free and combined bromine residual, it is possible that some combined bromine existed and was picked up by the amperometric method as "free residual." This has been suggested by Johannesson (19), Palin (11), and Sugam and Helz (16). Therefore, the so-called "free chlorine" residual measured by the standard amperometric method in estuarine or marine water is neither totally "chlorine" nor totally "free."

CHLORINATION PRACTICES

Chlorine dosage at many of the power plants was decreased during the course of this study. This was done both as a reaction to an awareness of greater than expected residuals and to decrease the residual in the discharge stream. Those plants using the OT method to set the chlorine dose were often chlorinating at twice the desired level because of the inaccuracies of the analytical method.

Total chlorine use per day for the four power plants located on the San Francisco Bay System averages about 0.30 metric tons/day (0.33 tons/day) based on 1971 figures (20). This represents 1.25% of the total average daily use of chlorine of 34 metric tons/day (37.5 tons/day) for the 1975-76 season as estimated by Russell and Horne (21) for the waste treatment plants discharging to San Francisco Bay.

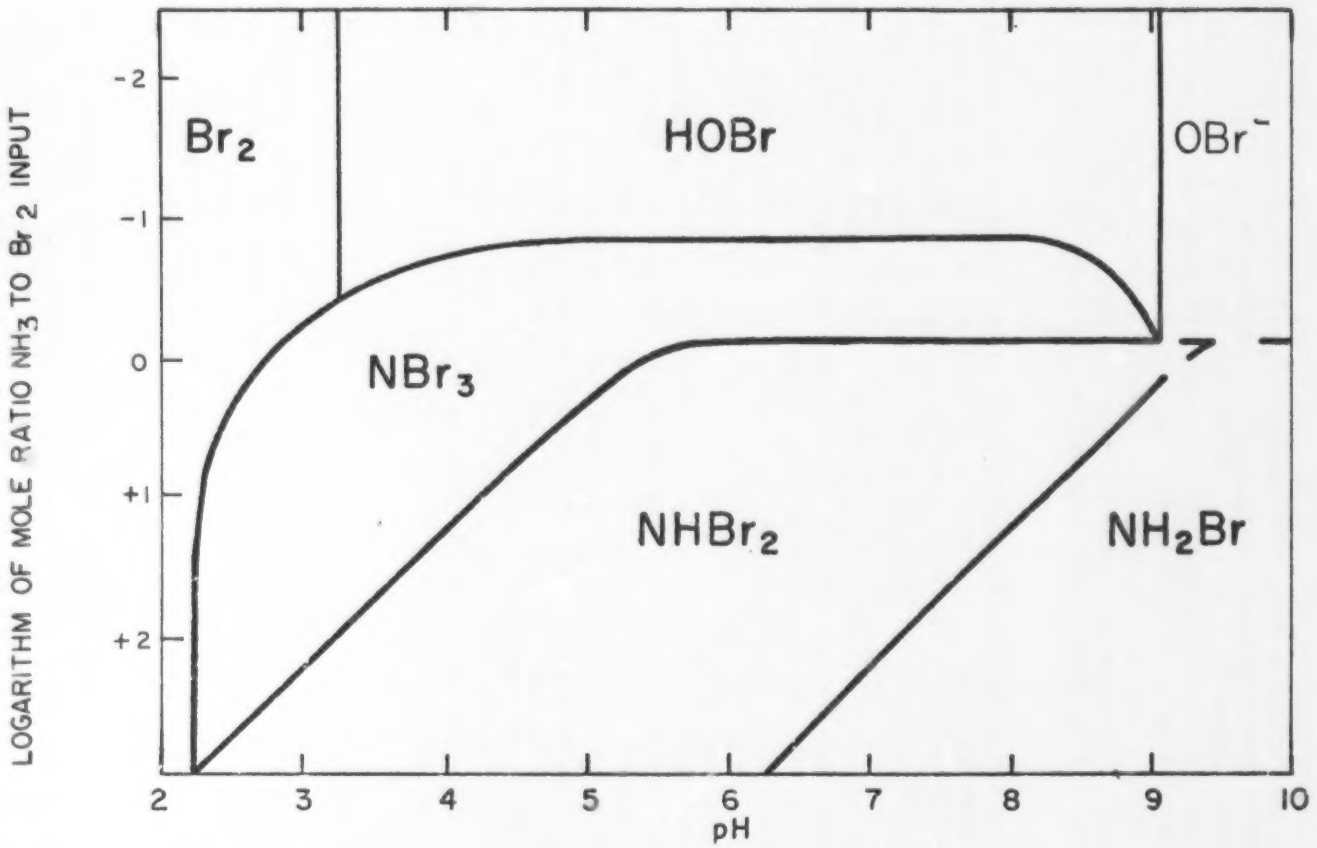

Figure 19. Principal species of bromine and bromamine after 1-2 min at various pH and ammonia to bromine ratios. Lines represent equal equivalent concentrations. Hypobromous acid separation from bromine given for 10^{-5} M bromide. (After Johnson and Overby [18]).

DEMANDS IN COOLING WATER SYSTEM

Table 9 and Figure 8 indicate that the loss of oxidant residual in the cooling water system was a function of flow time. The longer the cooling water was held within the plant, the lower was the oxidant residual that reached the receiving water. This loss of residual was due to many factors including reaction with ammonia-nitrogen, demand by inorganic reducing agents, reaction with organic nitrogen, and uptake by organisms living in the cooling water system. It is difficult to say which of these are the most important. Table 9 and Figure 8 suggests the flow time through the cooling water system may be a good method to estimate the oxidant residual to be expected at various locations from varying doses of chlorine.

DECAY AND RECEIVING WATER STUDIES

The decay studies (Figures 9-12, Table 10) show that the most persistent residual occurred at the Contra Costa Power Plant. From 50% to 52% of the 0.16 and 0.23 mg/ℓ TOR determined at the outfall remained after 60 min in those samples covered to exclude sunlight. From 38% to 39% of the 0.16 and 0.23 mg/ℓ TOR lasted for the same time period in samples exposed to sunlight. This persistence is likely explained by a slowly decaying combined chlorine residual that occurred at Contra Costa.

The highest concentrations of TOR remaining after 30 and 60 min were at Hunters Point and Potrero. However, this was due mostly to the greater initial concentrations of 0.43-0.72 mg/ℓ TOR. The lowest concentrations of TOR in decay studies were found at Moss Landing where the long flow time to the outfall sample point produced small initial TOR's of 0.22 and 0.20 mg Cl_2/ℓ. These were approximately the same initial TOR's which existed at the Contra Costa outfall, however the oxidant residual at Moss Landing decayed to much lower values. After 60 min at Moss Landing from 0.02 to 0.05 mgCl_2/ℓ remained while at Contra Costa from 0.06 to 0.12 mg/ℓ remained. The major difference between the oxidant residuals is the predominance of bromine residuals at Moss Landing which decay more rapidly than chlorine residuals (17,18,19).

The presence of sunlight appeared to speed up the rate of decay at all plants. This effect was most noticeable during the initial 20 min of decay at Contra Costa on 16 June 1976 when a FOR existed. After 20 min only combined residual existed and the effect of sunlight on decay became less pronounced. The significance of the oxidant residuals can be assessed in two ways. The first approach is to consider the effect on an organism such as a fish that is located at the discharge initially and then swims with a parcel of water away from the plume. The second method is to consider the effect on an organism that remains in one spot and is subjected to intermittent doses of chlorine. Such a case would be representative of benthic organisms located in the sediments overlain by the discharge.

The first approach has been addressed by Mattice and Zittel (3). Table 11 is derived from their data and shows several dose-exposure time combinations that result in acute toxicity; the chronic toxicity threshold is also indicated for marine and freshwater organisms. At Contra Costa the cooling water

discharge is into a canal that has an approximate residence time of 12 min. In the canal average TOR concentrations were on the order of 0.05 $mgCl_2/\ell$. According to Mattice and Zittel, this combination of chlorine dose and exposure time would not result in acute toxicity to freshwater organisms. It is very close to Mattice and Zittel's acutely toxic level for marine organisms. A TOR of 0.02 $mgCl_2/\ell$ was detected for a distance of some 150 m (500 ft) down the San Joaquin River. Assuming an average water velocity of 0.55 m/sec (1.8 ft/sec) this results in an exposure time of 4.6 min at this TOR concentration. This TOR level is at Mattice and Zittel's chronic toxicity level for marine organisms. For freshwater organisms the dose/exposure time stated to be acutely toxic to freshwater organisms by Mattice and Zittel is 0.02 mg/ℓ for 200 min.

TABLE 11. ACUTE AND CHRONIC DOSES OF CHLORINE TO MARINE AND FRESHWATER ORGANISMS (Mattice and Zittel) (3)

MARINE ORGANISMS		FRESHWATER ORGANISMS	
TOR $mgCl_2/\ell$	DURATION min	TOR $mgCl_2/\ell$	DURATION min
0.20	0.50	0.10	25
0.15	1.0	0.05	60
0.10	2.5	0.02	200
0.05	13	0.01	550
0.02*	--	0.0015*	--

*Chronic toxicity threshold.

Current velocities in the discharge plumes have been determined by PG&E at the Hunters Point and Potrero Plants. At Hunters Point the time to reach the 0.02 mg/ℓ TOR isoconcentration line is 45 sec. Assuming that the velocity is constant between the outfall and the 0.02 mg/ℓ TOR isoconcentration line, the estimated time to reach 0.05 mg/ℓ TOR is between 11-28 sec; with the same assumption, the time to reach the 0.10 mg/ℓ TOR isoconcentration line is 7 sec. These dose/exposure times are far below the values quoted by Mattice and Zittel to be acutely toxic to both freshwater and marine organisms. Concentrations of TOR exist in the receiving water that are above the chronic toxicity threshold for both freshwater and marine organisms.

At Potrero, with an average discharge concentration of 0.3 mg/ℓ TOR, the time to the 0.02 mg/ℓ TOR isoconcentration line is approximately 3 min. Using the same assumptions as for Hunters Point, the time to the 0.1 mg/ℓ TOR isoconcentration line is estimated to be between 48-56 sec; from the 0.1 mg/ℓ

TOR to the 0.05 mg/ℓ TOR isoconcentration line is between 20-65 sec. The exposure between the 0.3 mg/ℓ TOR discharge and the 0.1 mg/ℓ TOR isoconcentration line (assumed to be an average of 0.2 mg/ℓ TOR) is predicted to be acutely toxic to marine organisms. Acute toxicity is not predicted according to the Mattice and Zittel data beyond this area. Chronic toxicity to marine organisms is predicted to exist out to the 0.02 mg/ℓ isoconcentration line and considerably further for freshwater organisms.

The 0.16 mgCl_2/ℓ maximum concentration measured at the surface of Monterey Bay at the outfall from the No. 6 and 7 Units at Moss Landing could only have existed for a flow time of a few seconds from the discharge pipes located at a depth of 6.1 m (20 ft). At a distance of some 15.3 m (50 ft) from the discharge, a residual of 0.09 mgCl_2/ℓ was detected. For this residual to be acutely toxic by Mattice and Zittel's criterion, an exposure time of some 2.5 min must exist. It is questionable whether such a contact time existed between the discharge structure and a point some 50 ft away on the surface. These chlorine levels are above those suggested by Mattice and Zittel as chronic toxicity threshold values for both freshwater and marine organisms.

The second approach has been investigated by Dickson et al. (22) who studied the effects of intermittent chlorination on goldfish and on protozoans obtained from attached growths. LC-50 values for goldfish were found to be a function of total exposure time during a 24-hr period. In the temperature range of 17-22.5°C, 2-hr exposure/day resulted in an LC-50 of 1.18 mg/ℓ TOR; with 3-hr exposure the LC-50 was 0.[illegible] TOR and with 4-hr/day exposure the LC-50 fell to 0.63 mg/ℓ TOR. These [illegible] concluded that 2-3 exposures of 15-30 min/day at a TOR of 0.5-0.75 mg/ℓ did not result in lethality to the goldfish. Concentrations in the ranges stated above were never detected in the receiving waters at any location sampled during this study. Indeed, only in early studies at Hunters Point and Potrero, before the reduction in chlorine dosage by PG&E took place, were such levels detected in the outfalls. It might, therefore, be concluded that with current chlorination practice no lethality would result from chlorine toxicity in cooling water to fish with the same response as goldfish.

SECTION 5

CONCLUSIONS

CHLORINATION PRACTICE

1. Chlorination frequency varied among the five power plants studied from 1/week to 4/day. Duration of chlorination varied from 15 to 40 min per cycle.

2. Oxidant residual determined at the condenser inlets was the criterion used by the power plants to determine the level of chlorine dose.

3. During this study the chlorine dose to produce the desired residual of approximately 0.5 $mgCl_2/\ell$ at the condenser inlets was reduced. This reduction resulted from a more precise measurement of chlorine residuals throughout the cooling system that was afforded by the amperometric method used by us as compared to the OT method routinely used by power plant personnel.

4. All of the plants are currently using or are in the process of obtaining amperometric titrators due to more stringent regulations that require accurate measurement of oxidant residuals.

IN-PLANT STUDIES

5. Total chlorine usage per day for the four power plants located on San Francisco Bay averaged about 0.3 metric tons/day (0.33 tons/day) based on 1971 figures. This represented 1.25% of the total average daily use of 34 metric tons/day (37.5 tons/day) estimated for 1975-76 for waste discharges entering San Francisco Bay.

6. Oxidant residuals determined at the condenser inlets were often significantly higher than the 0.5 or 1.0 mg/ℓ desired by plant personnel, especially at those plants using the OT method for control of chlorine residual.

7. At Contra Costa, where the cooling water was the freshest, a combined residual of from 0.10 to 0.40 $mgCl_2/\ell$ existed from the condenser inlet to the outfall.

8. At Hunters Point, Potrero, and Moss Landing, where cooling water ranged from 79% to 99% seawater, total oxidant residual generally equalled free oxidant residual at the condenser inlets. Some combined residual

was detected at the outfall of Hunters Point and at a sample point 6-7 min of flow time from the condenser inlet at Moss Landing.

9. The DPD-FAS results indicated that most of the oxidant residual at Hunters Point and Moss Landing was bromine residual.

10. The disappearance of total oxidant residual through the cooling water system generally depended on the flow time. At Moss Landing where the total flow time in the system was 6 to 7 min, from 16% to 27% of the oxidant input remained at the outfall. At Potrero where the total flow time in the system was only 1.3 min, from 54% to 78% of the oxidant input remained at the outfall.

DECAY AND RECEIVING WATER STUDIES

11. The slowest decay at the outfall was observed at Contra Costa where 50% to 52% of the total oxidant residual of 0.18-0.23 mg/ℓ measured at the outfall remained after 60 min in the samples covered to exclude sunlight. For the samples exposed to sunlight, 38% to 39% remained after the same time period.

12. The most rapid decay at the outfall was observed at Hunters Point where 17% to 28% of the total oxidant residual of 0.52-0.72 mg/ℓ measured at the outfall remained after 30 min in the samples covered to exclude sunlight. For the samples exposed to sunlight, only 6% to 17% remained after the same time period.

13. Maximum total oxidant residuals were found to exist at the surface of receiving waters likely because of the natural buoyancy of the warmer effluent.

14. During the chlorination cycle at Contra Costa, an 0.02 mgCl_2/ℓ residual was measured some 150 m (500 ft) from the point where the discharge canal meets the San Joaquin River.

15. During the chlorination cycle at Hunters Point, 0.02 mgCl_2/ℓ residual was measured up to 150 m (500 ft) from the No. 4 outfall and up to 168 m (550 ft) away from the No. 3 outfall at Potrero, and up to 400 m (1300 ft) from the No. 1 and No. 2 outfall at Potrero.

16. A maximum residual of 0.16 mgCl_2/ℓ was measured at the surface of Monterey Bay above the outfall from the No. 6 and No. 7 Units at Moss Landing.

17. Using the approach of Mattice and Zittel, it was determined that all effluents produced receiving water oxidant residual levels that would be predicted to demonstrate chronic toxicity to marine organisms; the receiving water from two plants (Hunters Point and Moss Landing) showed levels that would be predicted to demonstrate chronic toxicity to freshwater organisms. Acutely toxic levels to freshwater and marine organisms existed in the receiving waters at the Potrero site.

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APPENDIX I

FIELD DATA

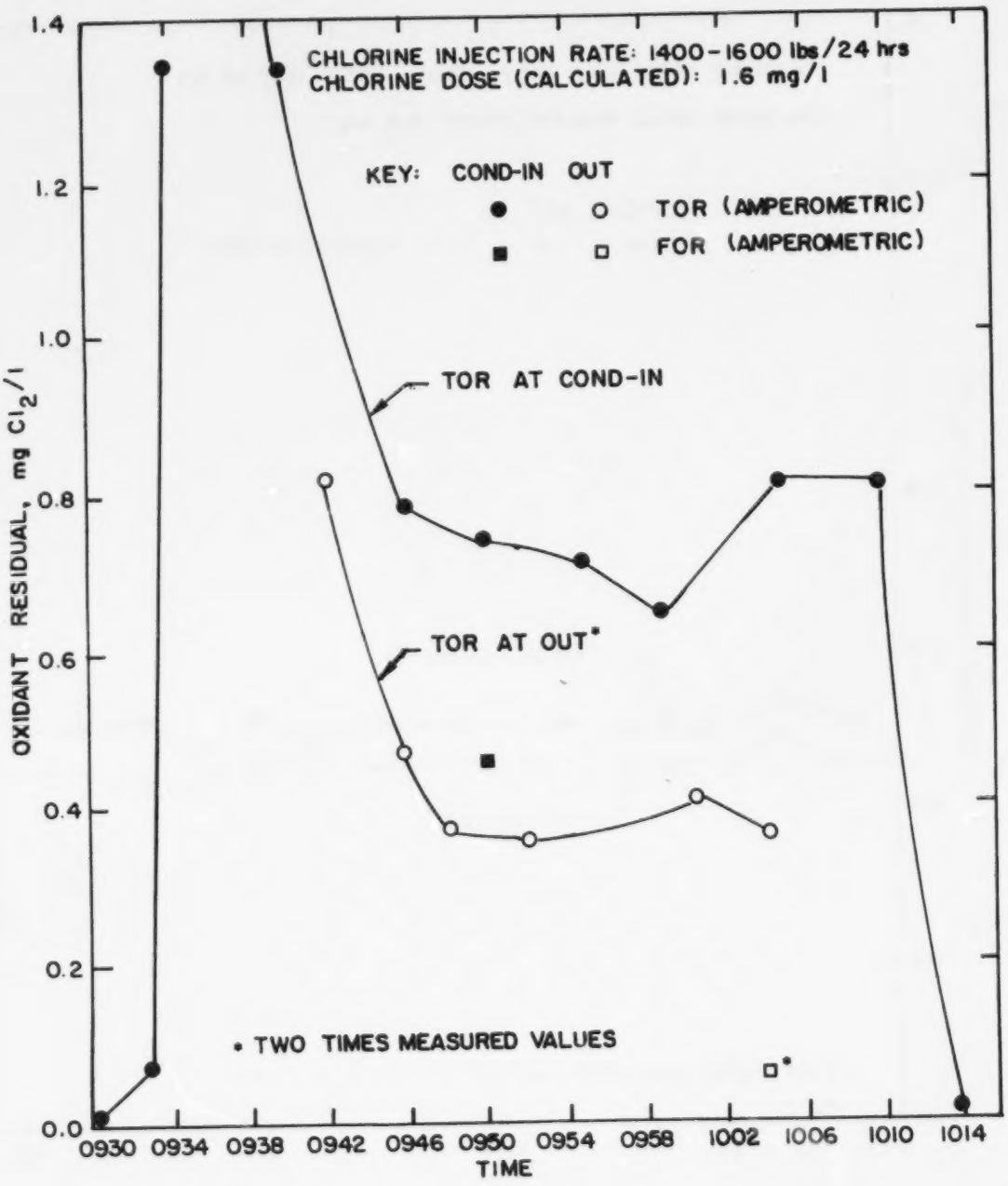


Figure 20. In-plant Study at the Contra Costa Power Plant 20 Jan 1976, Unit 6, Condenser #11.

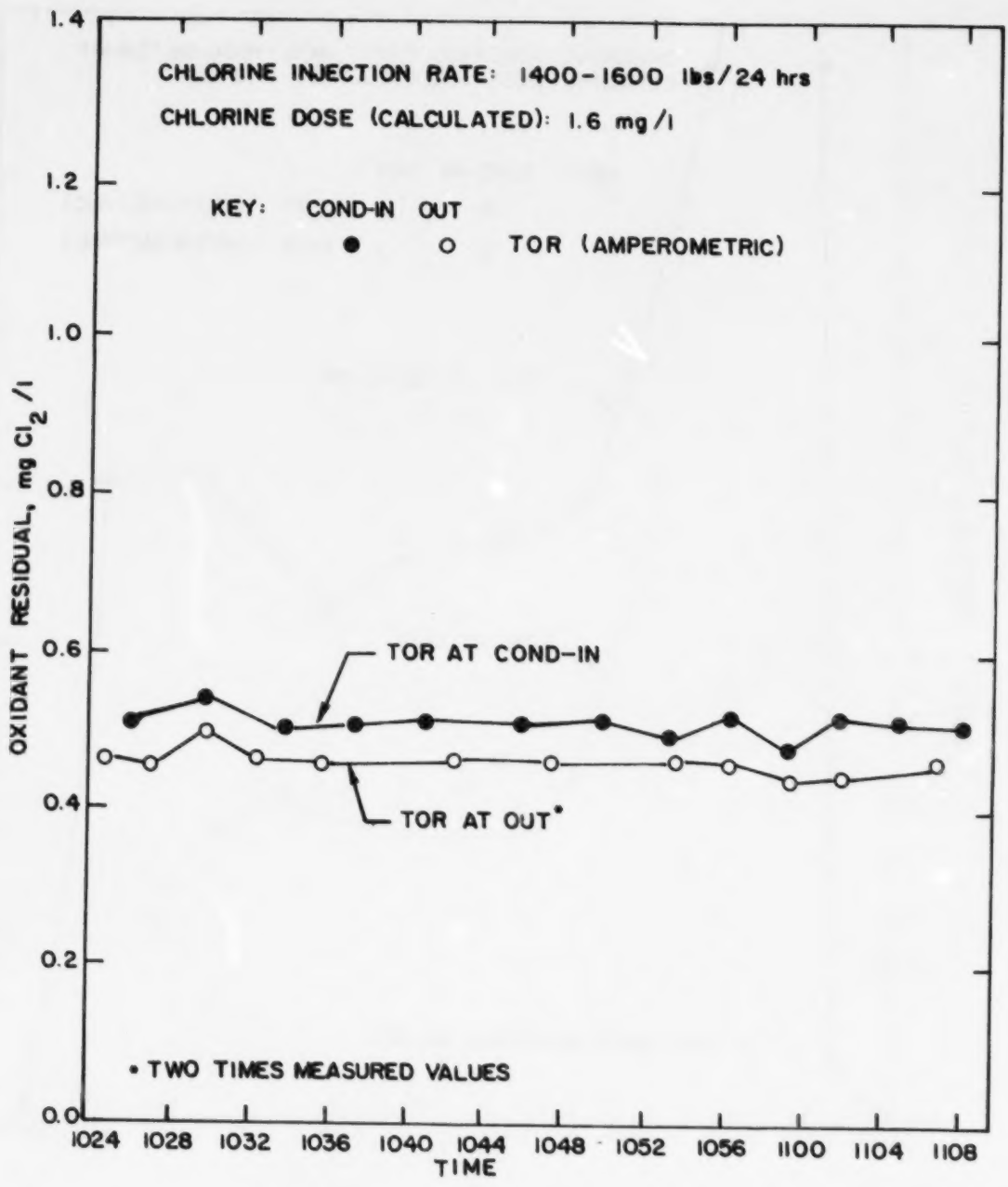


Figure 21. In-plant Study at the Contra Costa Power Plant 10 Feb 1976, Unit 7, Condenser #14.

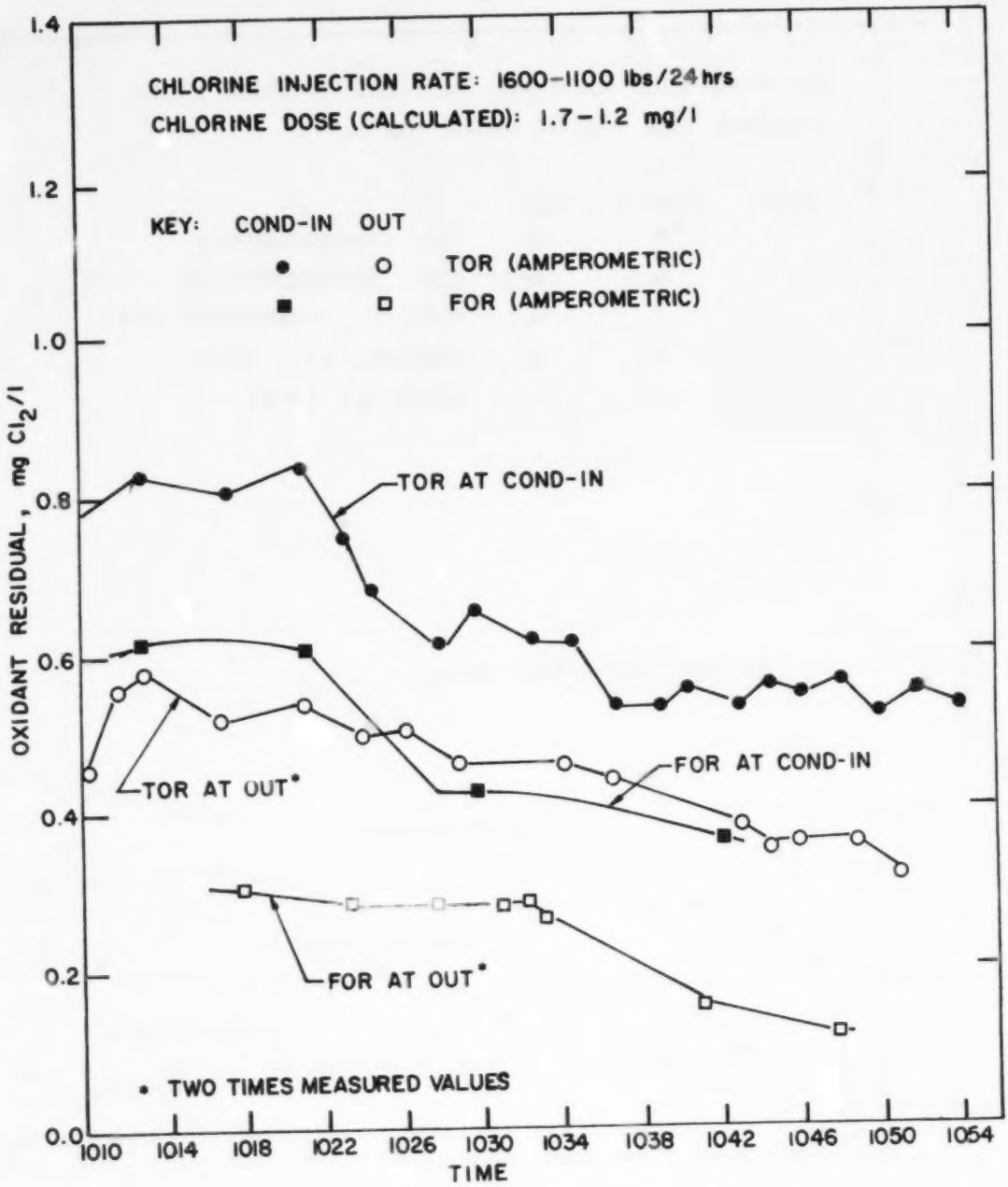


Figure 22. In-plant study at the Contra Costa Power Plant 6 Jun 1976, Unit 7, condenser #13

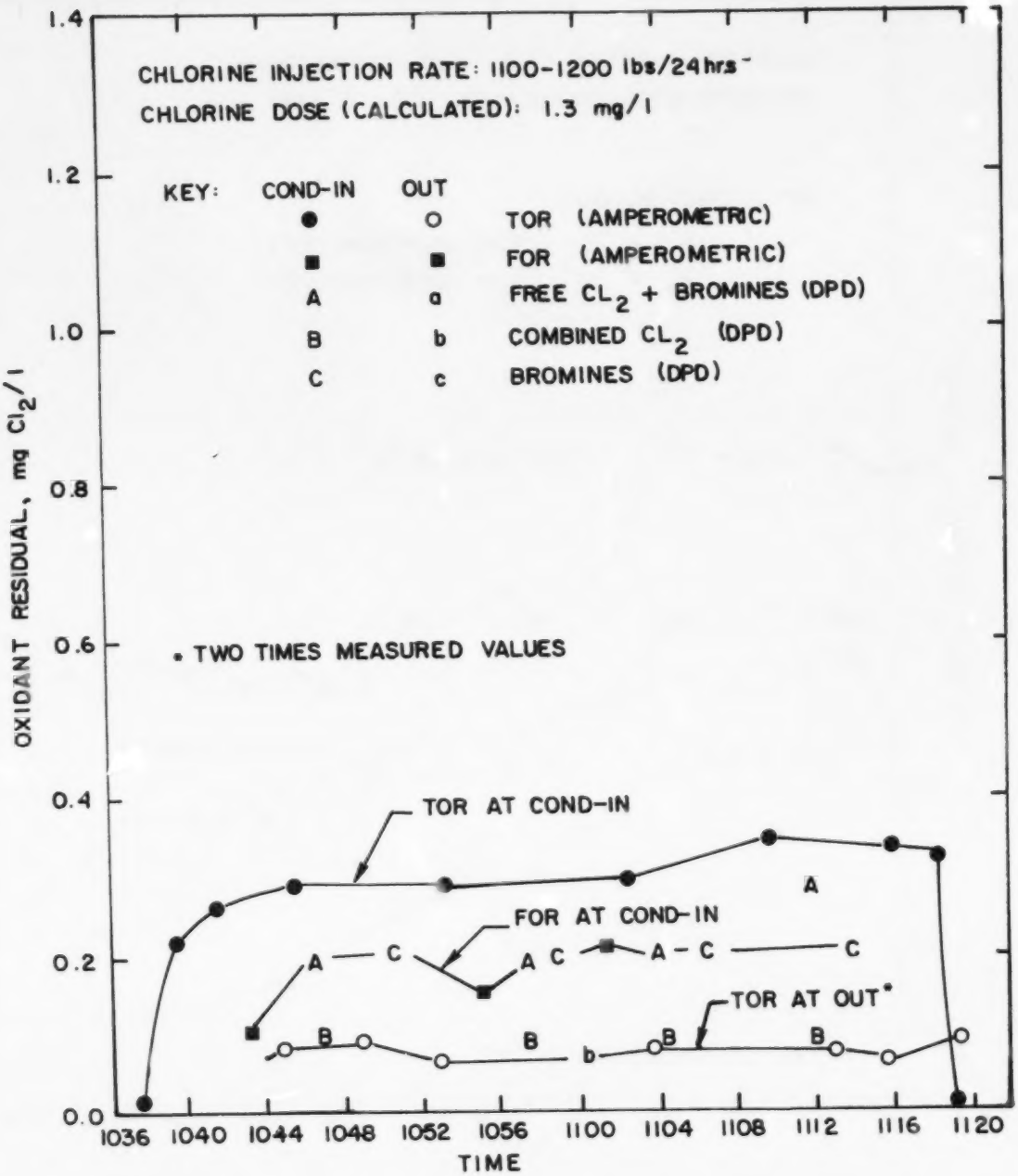


Figure 23. In-plant Study at the Contra Costa Power Plant 14 Sept 1976, Unit 6, Condenser #11.

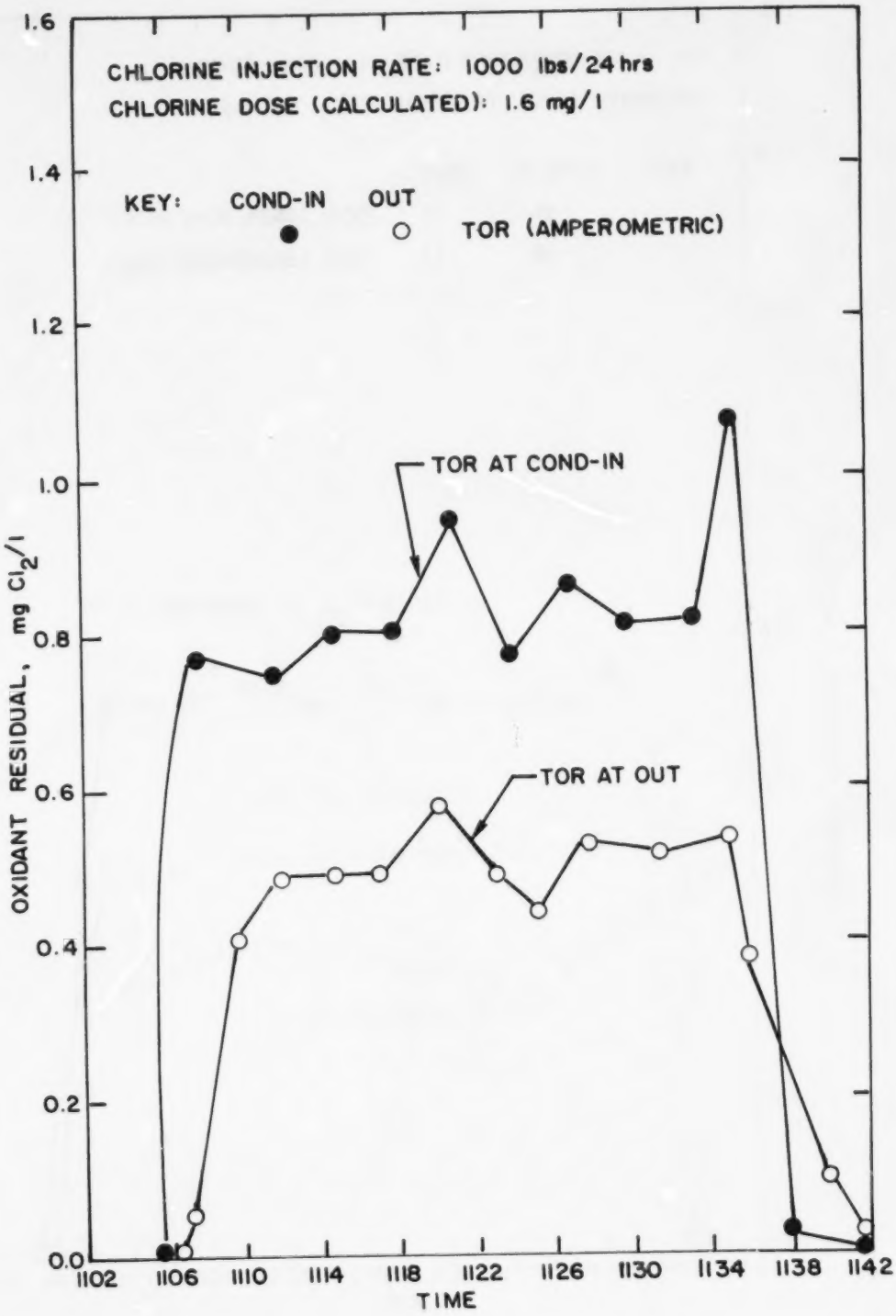


Figure 24. In-plant Study at the Hunters Point Power Plant,16 Dec 1975, Unit 4.

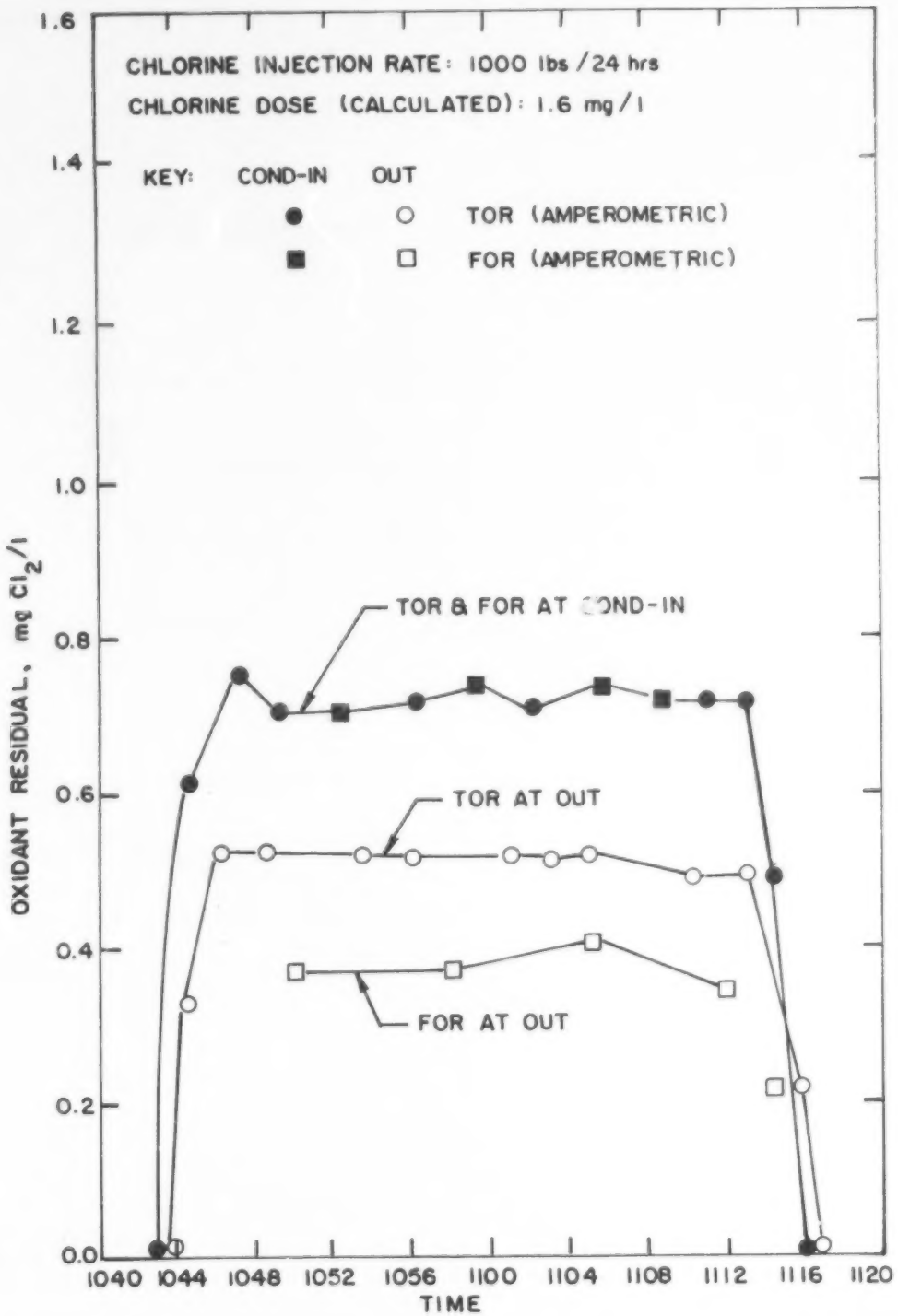


Figure 25. In-plant Study at the Hunters Point Power Plant 17 May 1976, Unit 4.

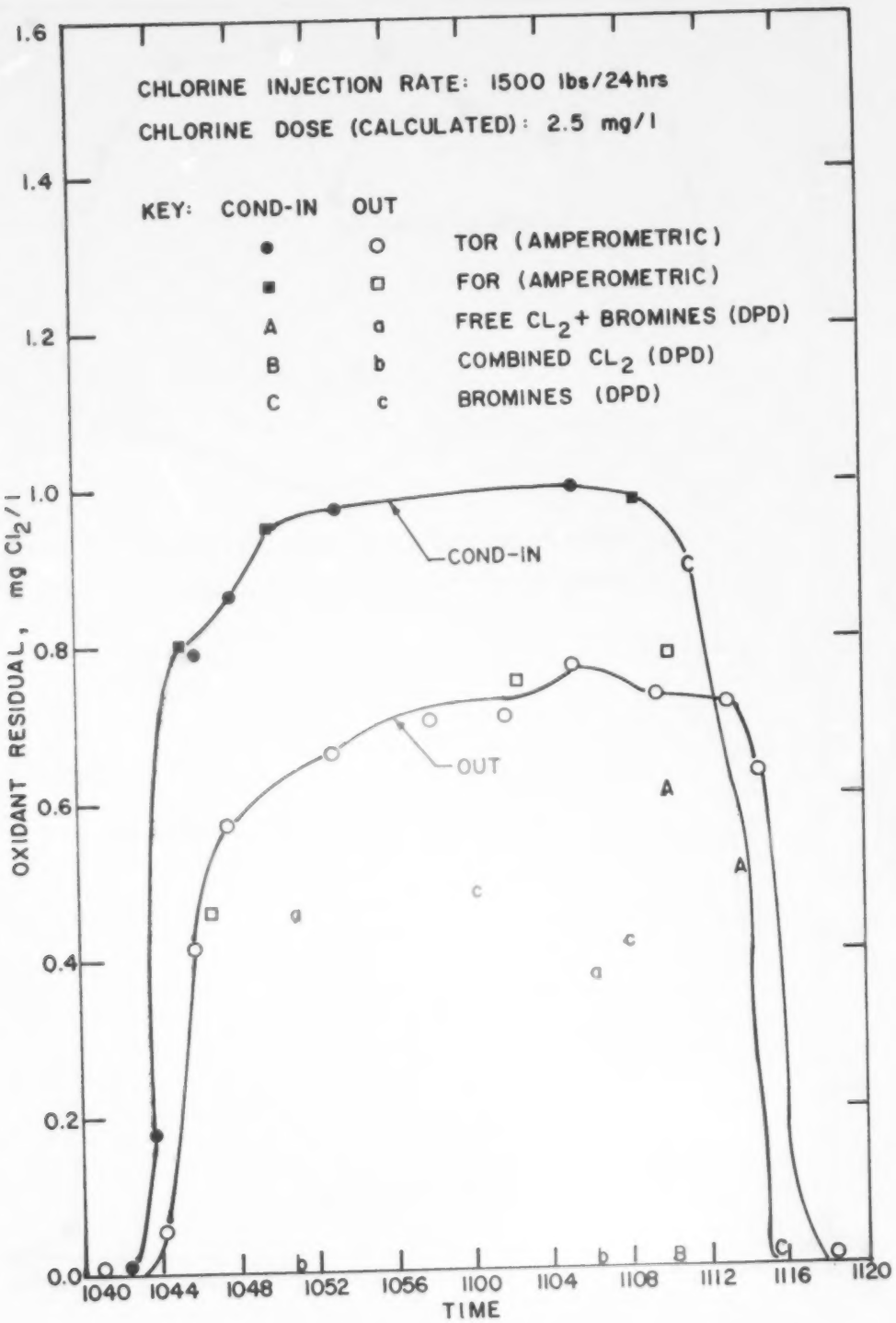


Figure 26. In-plant study at the Hunters Point Power Plant, 26 August 1976, Unit 4

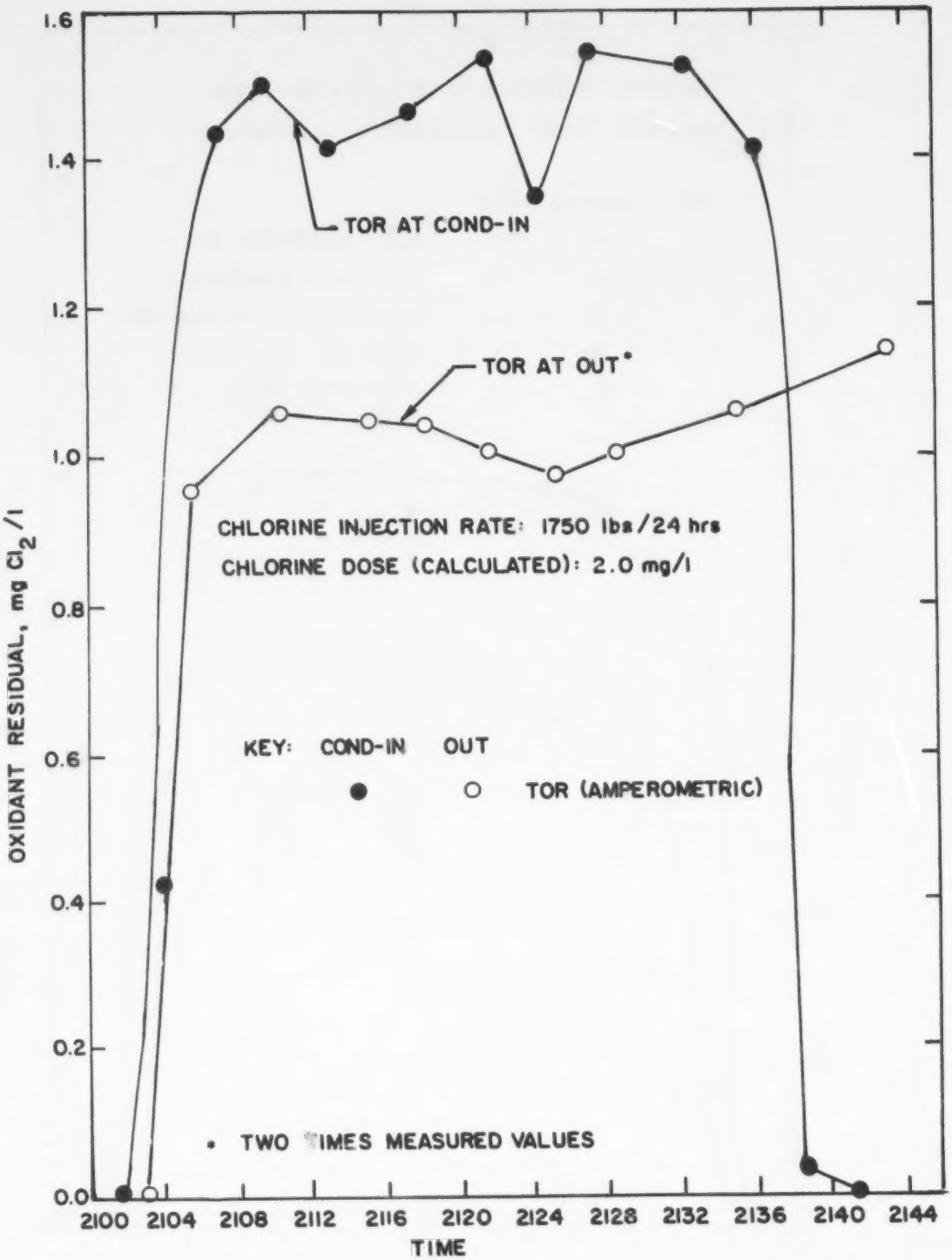


Figure 27. In-plant Study at the Potrero Power Plant
23 Feb 1976, Unit 3, N. Condenser.

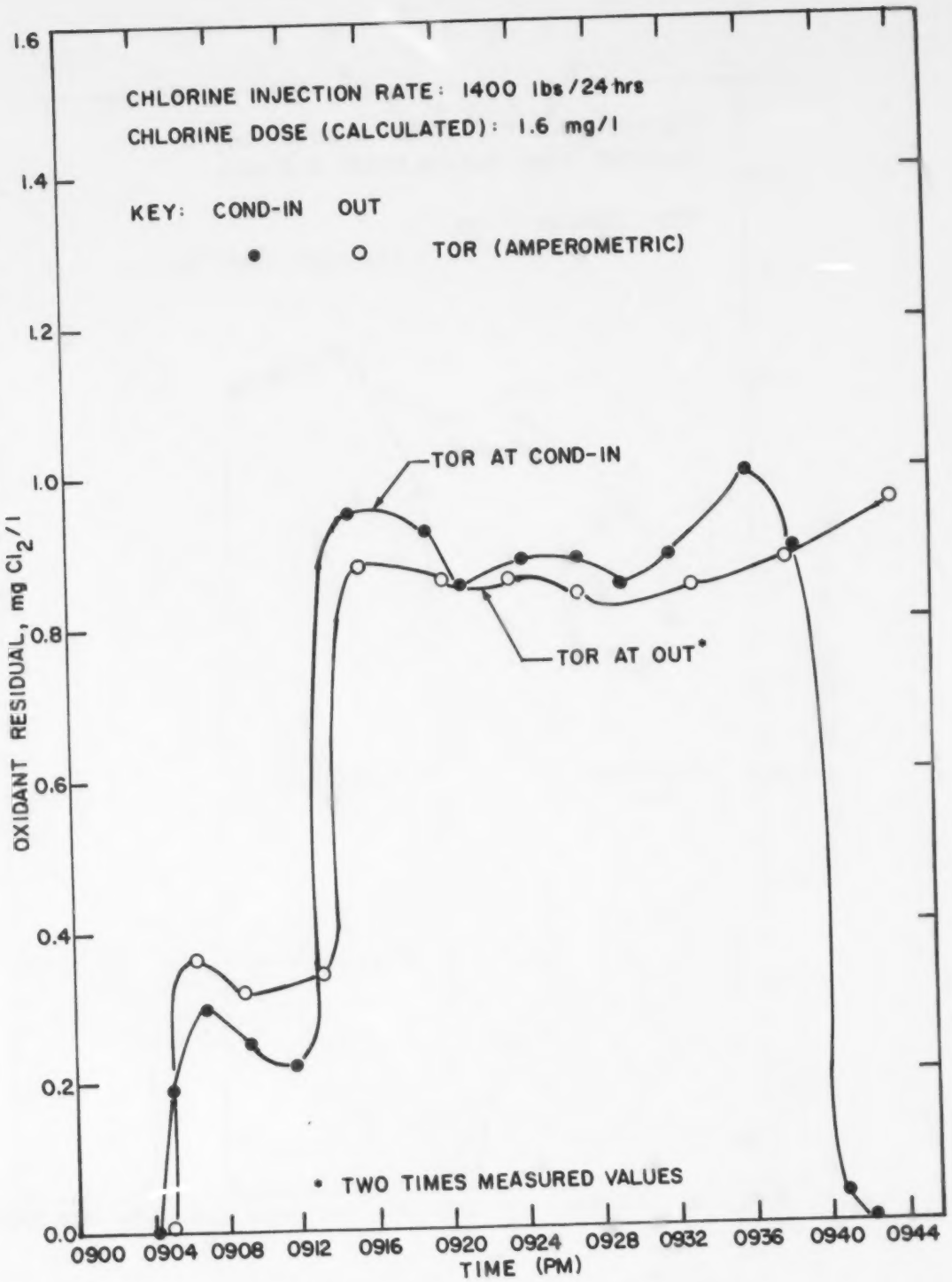
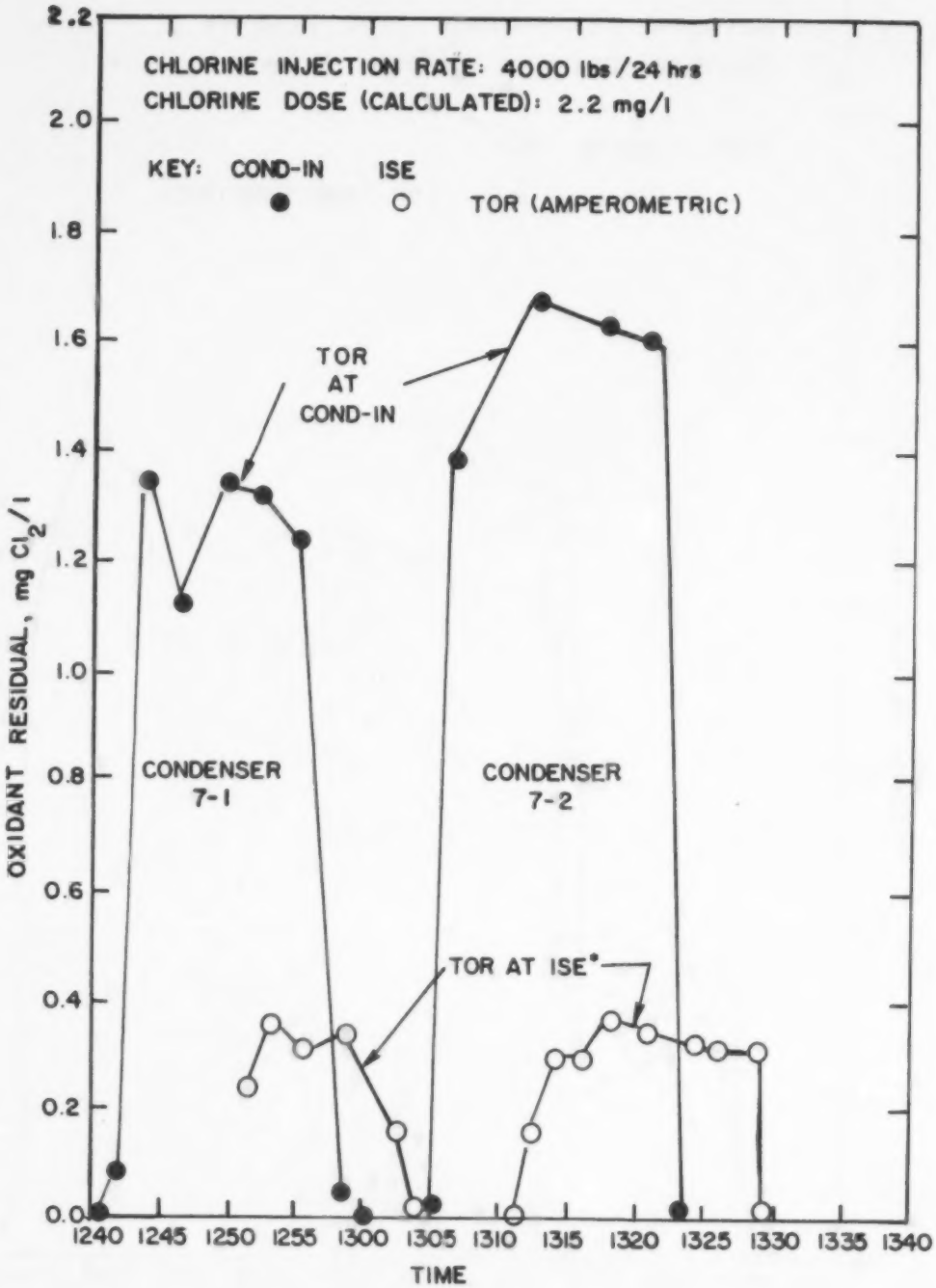
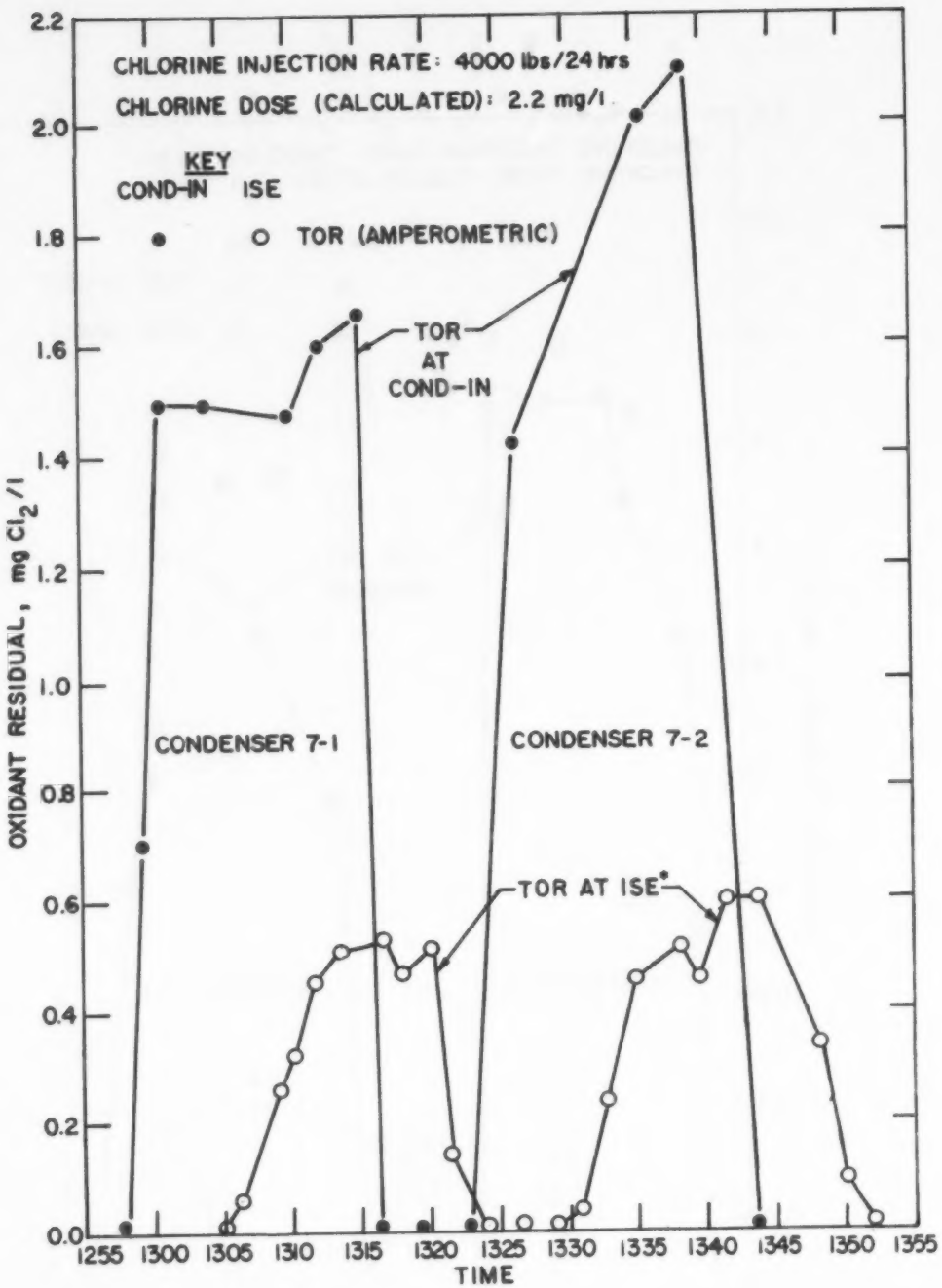


Figure 28. In-plant study at the Potrero Power Plant, 4 March 1976, Unit 3, N. Condenser



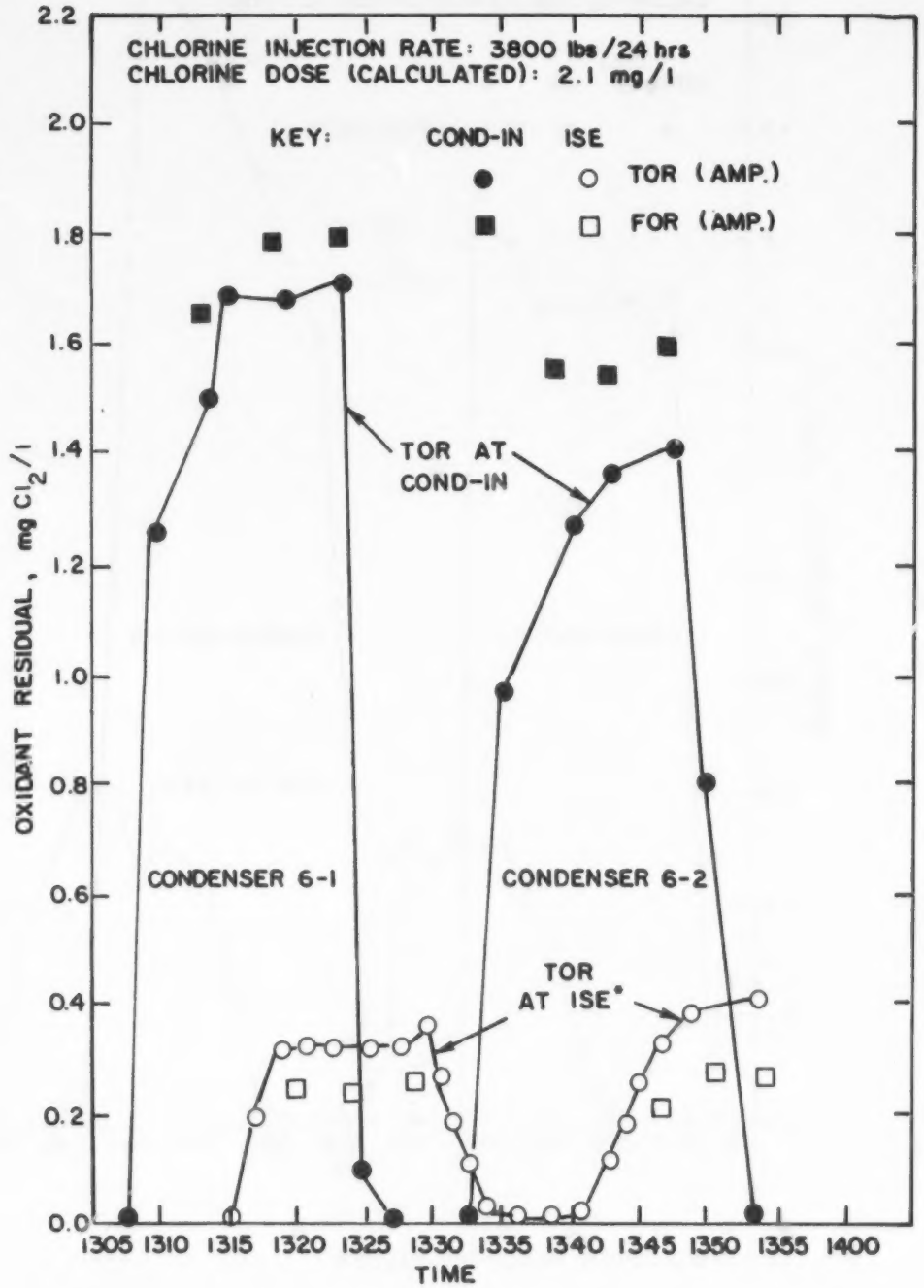
* TWO TIMES MEASURED VALUES

Figure 29. In-plant Study at the Moss Landing Power Plant 12 April 1976, Unit 7.



* TWO TIMES MEASURED VALUES

Figure 30. In-plant study at the Moss Landing Power Plant, 19 April 1976, Unit 7



* TWO TIMES MEASURED VALUES

Figure 31. In-plant Study at the Moss Landing Power Plant 14 July 1976, Unit 6.

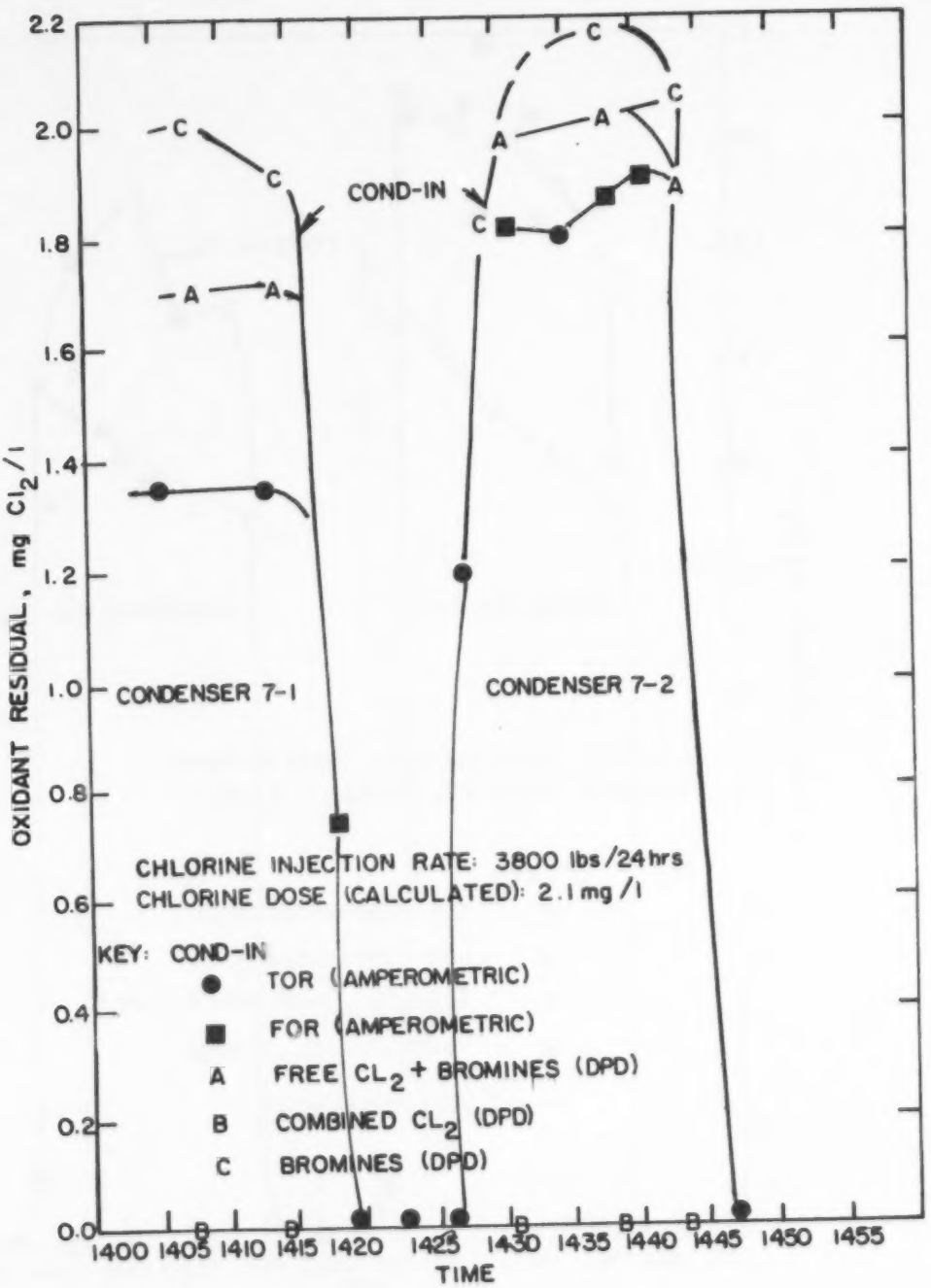


Figure 32. In-plant Study at the Moss Landing Power Plant 14 July 1976, Unit 7.

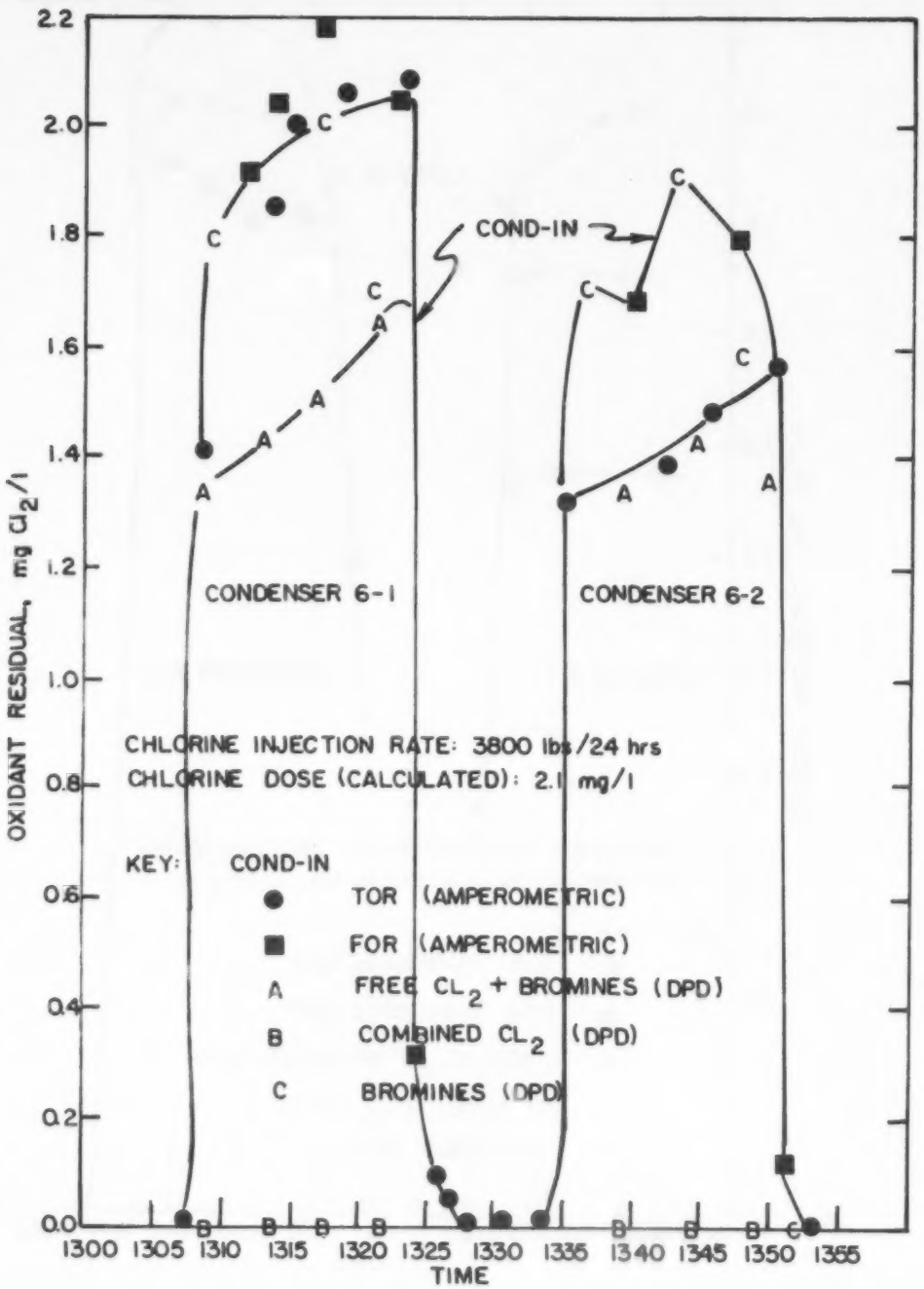


Figure 33. In-plant Study at the Moss Landing Power Plant 22 July 1976, Unit 6.

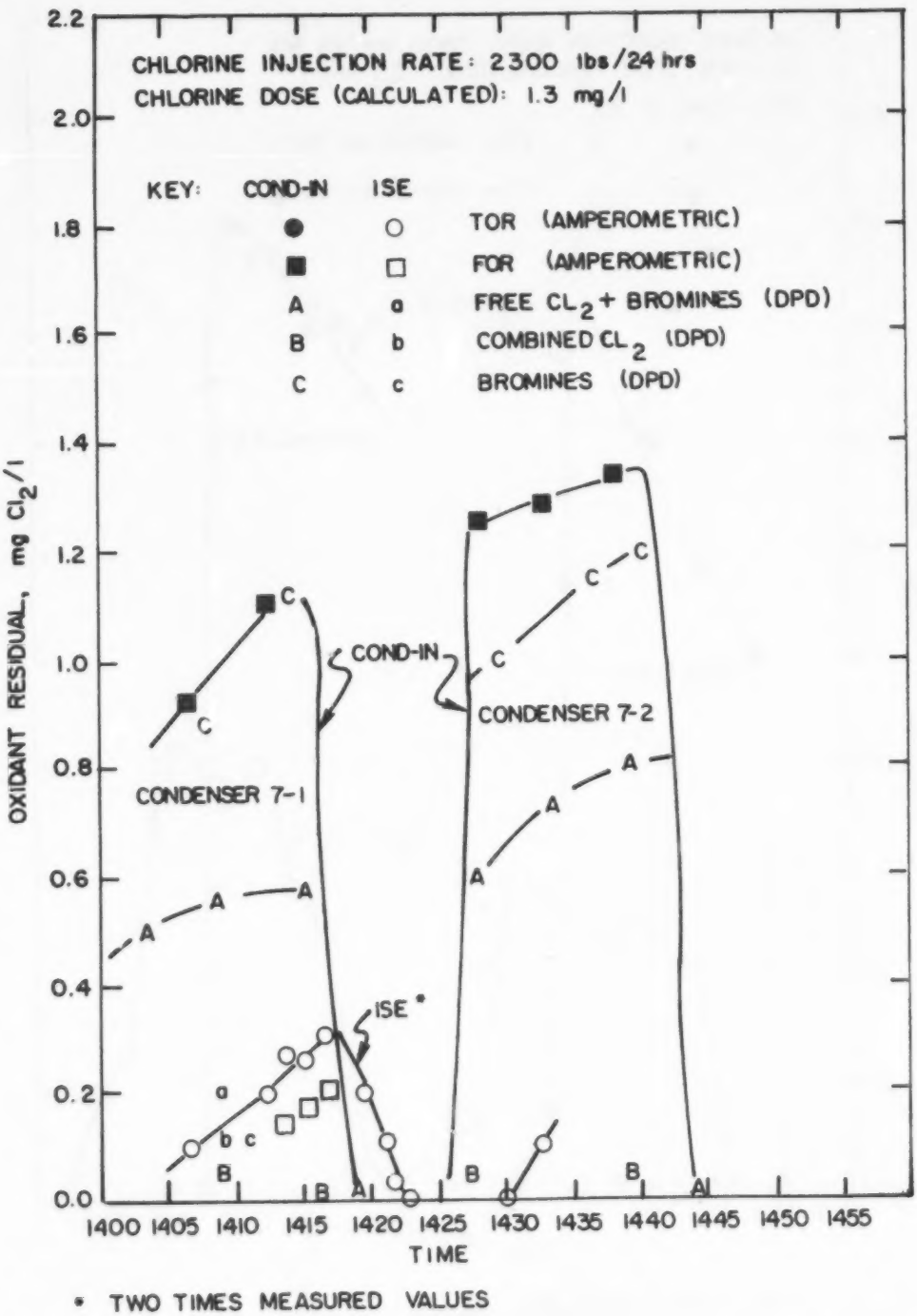
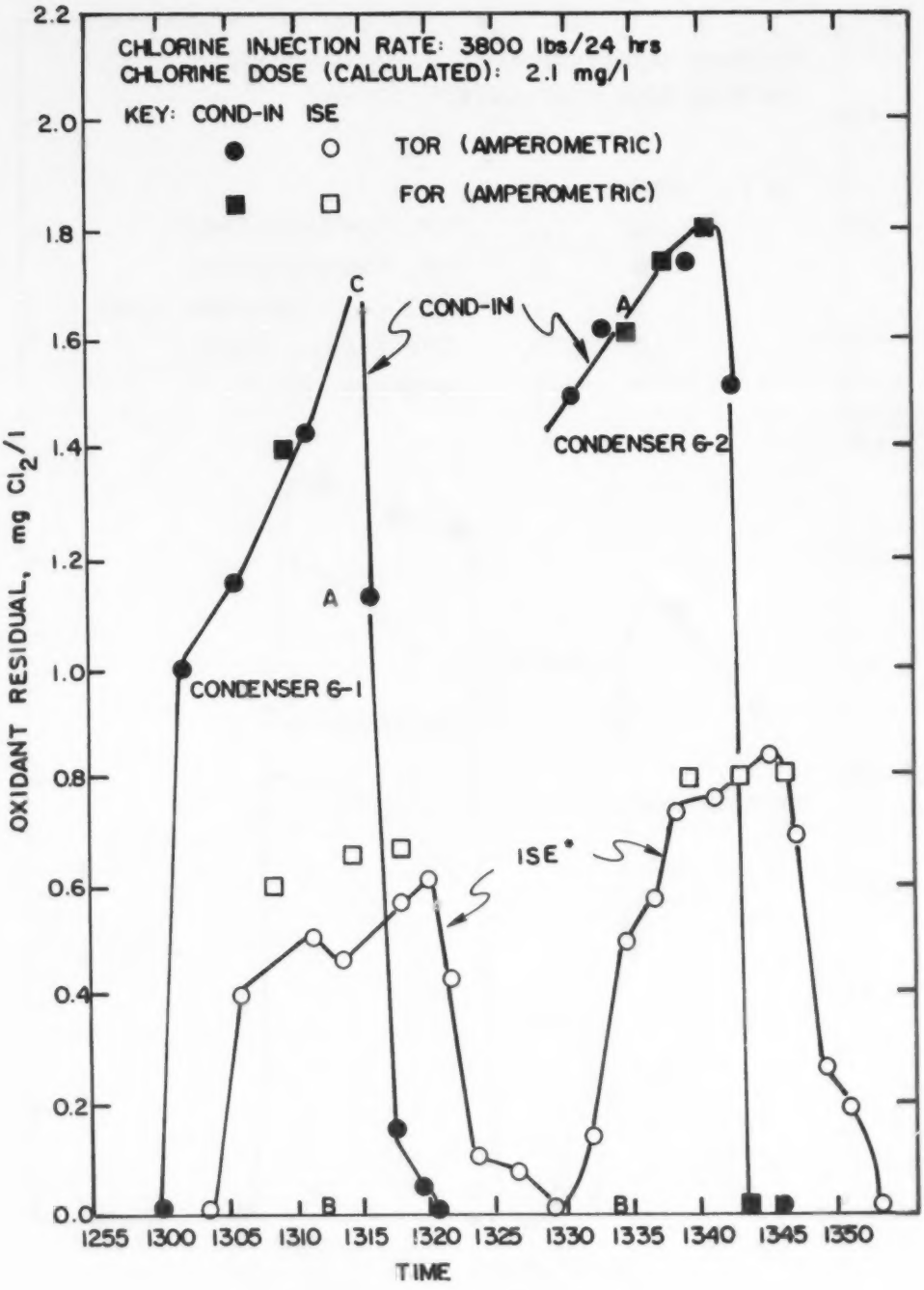


Figure 34. In-plant Study at the Moss Landing Power Plant 5 August 1976, Unit 7.



• TWO TIMES MEASURED VALUES

Figure 35. In-plant Study at the Moss Landing Power Plant 23 Sept 1976, Unit 6.